

Procedures for geochemical analysis of tholeiitic basalts: XRF, ICP-MS, MC-ICP-MS, TIMS and EPMA

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1 Introduction

The typically low concentrations of Pb in tholeiitic basalts, means that it is particularly sensitive to sample contamination, both from when it was exposed to the elements in the field and from particulate matter that can attach during handling in the lab. The need to obtain high quality Pb isotopic analyses is therefore the governing factor when drawing up procedures to take the rocks from sample bag to mass-spec.

These procedures are written for making Nd and Pb measurements on an MC-ICP-MS, specifically the Nu Plasma instrument in Cambridge. The effect of Krypton interference on Sr measurements with MC-ICP-MS, derived from an impure Argon source, mean that Sr is run separately on the TIMS machine. The implications of using TIMS over MC-ICP-MS for the chemistry of Sr separation are that organic resins are avoided

The lab book is written using information contained in the LDEO lab book (Ide, 2003), the work of Sarah Nixon (2009) and David Wilson (2008) who developed procedures in Cambridge, and discussion with scientists in and out of Cambridge.

2 Crushing and powdering

Notes

- The basement is dusty and dirty, everything should be done to minimise chances that particulate matter is combined with the samples.
- During crushing a lot of dust can be produced, only ever have one sample bag in the room at a time, clean the room before bringing the next sample in.
- Keep the time samples are exposed to the air to a minimum, and try and work quickly.
- Try and use as large a sample size as possible, this way any potential contamination has minimum impact on bulk composition.
- IMPORTANT: Do not use the air compressor. It can eject a fine mist of oily water. Leave objects to air dry.

2.1 Hand Crushing: To obtain whole-rock chips

Aim

To obtain fresh, phenocryst free, millimetre sized chips of basalt for dissolution. This method should be used to obtain sample material for Sr-Nd-Pb isotopic analyses.

2.1.1 Procedure

1. Clean down rock crushing room.

Ventilate the room.

Sweep and Hoover floor.

Scrub bench surface.

Scrub rust off hand crusher base and hammer (could use wire wool, but in this case make sure to clean away metal fibres afterwards.)

Clean plastic surround to hand crusher.

Clean hand brush.

2. Find portion of rock to crush. Avoid:

Dust/mud filled vesicles.

‘Rust’ filled vesicles.

Portions of the rock where the olivine crystals are an oily colour.

Chips from the cut face of a rock.

Rock from near the weathered margins of the rock.

3. Once crushed, pick out (using plastic coated tweezers) a few tens of chips on the basis that they are phenocryst free, unaltered and clean.
4. Brush remaining crush from base into *empty* sample bag, do not recombine with original whole rock sample.
5. Clean base, hammer, plastic surround, bench surface, brush and tweezers, using clean paper towels.

2.2 Machine Crushing: To obtain whole-rock chips

Aim

To obtain fresh, millimetre sized chips of basalt. Use this method if the sample material is going to be analysed for elemental concentrations.

2.2.1 Procedure

1. Clean down rock crushing room.

Ventilate the room.

Sweep and Hoover floor.

Scrub bench surface.

2. Clean the rock crusher.

Take the two jaw plates off of the rock crusher and scrub clean. Use a green scrubbing brush, run the jaws under the tap once scrubbed, then dry down with paper towel.

Empty and scrub clean the plastic sample collection tray, then dry with paper towel. Leave overturned on side to dry.

Sweep away all dust from the inside of the jaw crushing machine, paying particular attention to the gaps between the parts the jaw plates rest on and the surrounding metal, and the tops of the exterior surfaces just above the jaws.

Replace the jaws, close the machine, and start it running for a few seconds.

Take out the whole sample collection drawer and empty the dust collected in it.

Replace the plastic tray in the drawer and reinsert the drawer beneath the machine, checking again to see if any dust dislodges itself into the drawer.

3. Start the machine and add the sample, touching it as little as possible.
4. After the grinding has finished, remove the plastic tray and decant the sample into a sample bag.

2.3 Powdering samples

Aim

To obtain a very fine powder of sample material, ready for dissolution for ICP-MS and making disks for XRF.

Notes

- Frequently wash hands during powdering. Always wash hands between touching different sample cells and sample bags.
- Never have more than one sample open to the atmosphere at one time, and always close and store empty agate cells/glass vials away from the work bench.
- Avoid touching the bases of the agate cells, or allowing the cells to come into direct or indirect contact with sample.

2.3.1 Procedure

1. Clean rock powdering room.

Ventilate the room.

Sweep and vacuum floor.

Scrub bench surface.

Vacuum inside the rock powdering machine.

2. Clean the agate grinding cell and agate balls. Scrub the inside and lid of container with green scrubbing cloth, wipe clean with paper towel, leave to air dry.
3. Pre-contaminate the agate cell: Pour a small fraction of the sample into the agate cell and place in grinding machine for **5 minutes** at **250 rpm**.
4. Unload sample onto clean A4 sheet of paper, pouring powder to waste, but avoid touching the agate cell and balls as much as possible.
5. Load sample into the pre-contaminated agate cell. The maximum sample load is the level just below the top of the first layer of agate balls.
6. Place cell in grinding machine and tighten clamps securely. Set to **250 rpm** and leave to run for **15 minutes**.
7. Unload the samples one at a time, carefully pouring onto a lightly pre-creased sheet of clean A4 paper, being careful to keep the agate balls from rolling off.
8. Store the powdered sample in labelled glass vials.
9. Move sample vial and agate cell away from the working bench area, wipe down the surface, clean hands and repeat for remaining samples.

Part I

Isotopic analysis by MC-ICP-MS and TIMS

3 Cleaning of Lab Materials

This section is written assuming that equipment needs to be cleaned to the requisite standard to accurately measure Pb isotopes.

3.1 Cleaning procedure for new Savillex vials

416/N10:

1. Check the inside of the vials and lids for scratches. If there are any they may need to be rejected.
2. Rinse lids and vials three times in DI water.
3. Place in beaker containing 1% Decon solution.
4. Sonicate the beaker for 50 minutes.
5. Rinse vials, lids and beakers 3x with DI water.
6. Sonicate vials in DI water for further 50 minutes.
7. Rinse vials, lids and beaker 3x with DI water.
8. Place vials in clean zip-seal bag for transferal to 405a.

405a:

1. Dispose of plastic bag that contained vials.
2. Rinse vials and lids 3x in MQ water.
3. Soak in $\sim 50\%$ **conc.** reagent grade HCl, at least overnight, at 85°C - Ensure that no pockets of air are trapped in upturned vials or lids.
4. Once finished soaking, pour the acid back into the beaker from which it was taken.
5. Refill the tub with MQ water, covering the vials and lids, and pour the dilute acid solution down the sink. Perform this step twice to remove all acid from the vials.
6. Remove the vials and lids and rinse 3x with MQ water.
7. Soak vials and lids in $\sim 50\%$ **conc.** reagent grade HNO_3 overnight on the hotplate at 85°C .
8. Once finished soaking, pour the acid back into the beaker from which it was taken.
9. Refill the tub with MQ water, covering the vials and lids, and pour the dilute acid solution down the sink. Perform this step twice to remove all acid from the vials.
10. Rinse vials and lids 3x with MQ water.
11. Shake off any excess water.
12. Add a small amount of **6 N QD HCl** to each vial, just enough to cover the base.
13. Screw lids on tightly and place on hotplate at 85°C for at least **1 hr**.

14. Whilst the acid is still hot, uncap the vials and pour the acid away.
15. Rinse vials and lids 3x with MQ water.
16. Leave vials and lids to dry on tissues in the dry-down box. Place the lids and vials on their sides, so as to avoid particles settling into them.
17. Once the vials are dry, tightly cap them and place in storage in a clean plastic bag which details the cleaning procedures used.

3.2 Cleaning procedure for dirty Savillex vials

Always performed in 405a:

1. Check the inside of the vials for scratches/dirt. If there is any damage or dirt that can't be removed the vials should not be used.
2. Rinse vials and lids 3x with MQ water.
3. With a paper tissue over fingertip scrub the inside of the vial. Repeat this until the water pours from the vial without catching on the bottom.
4. Rinse the vials 3x more.
5. Soak in $\sim 50\%$ **conc.** reagent grade HCl, at least overnight, at 85°C - Ensure that no pockets of air are trapped in upturned vials or lids.
6. Once finished soaking, pour the acid back into the beaker from which it was taken.
7. Refill the tub with MQ water, covering the vials and lids, and pour the dilute acid solution down the sink. Perform this step twice to remove all acid from the vials.
8. Remove vials and lids and rinse 3x with MQ water.
9. Soak vials and lids in $\sim 50\%$ **conc.** reagent grade HNO_3 overnight on the hotplate at 85°C .
10. Once soaked overnight, pour the acid back into the beaker from which it was taken.
11. Cover the vials and lids with MQ water and pour the now diluted acid solution down the sink. Perform this step twice to remove all acid from the vials.
12. Rinse vials and lids 3x with MQ water.
13. Shake off any excess water.
14. Add a small amount of **6 N QD HCl** to each vial, just enough to cover the base.
15. Screw lids on tightly and place on hotplate at 85°C for at least **1 hr**.
16. Whilst the acid is still hot, uncap the vials and pour the acid away.
17. Rinse vials and lids once with MQ water.
18. Flick the vials dry, tightly cap them and place in storage in a clean plastic bag which details the cleaning procedures used.

3.3 Cleaning procedure for microcentrifuge tubes

1. Rinse the microcentrifuge tube lids and insides 3x with MQ water.
2. Acid clean in 10% **QD HNO_3** overnight, do not put on a hotplate. Use a pipette to ensure the HNO_3 reaches the bottom of the tube and that the lids are covered.
3. Rinse 3x with MQ water following dilute nitric soak, and place in drying cupboard.

3.4 Cleaning procedure for 15 ml and 50 ml centrifuge tubes

To clean 10 centrifuge tubes requires ~ 150 ml 20% HNO_3 , to make this amount and concentration of HNO_3 , add 30 ml 16 N HNO_3 to 120 ml MQ water.

1. Rinse the tube lids and insides 3x with MQ water.
2. Acid clean in **20% QD HNO_3** overnight at **40°C**.
3. Take off the hotplate and stand the correct way up, leave for 12 h.
4. Following the dilute nitric soak rinse 3x with MQ water, and place in drying cupboard.

3.5 Cleaning procedure for new column caps

1. Rinse the column caps 3x with MQ water, scrub the inside with a kimwipe and rinse one further time.
2. Acid clean in **10% QD HNO_3** overnight, do not put on a hotplate.
3. Rinse 3x with MQ water following dilute nitric soak, and place in drying cupboard.

3.6 Cleaning procedure for pipette tips

Notes

Avoid touching the pipette tip with the gloves, and try not to allow water to run off of your gloves onto the pipette tip.

1. Remove the pipette tip from the container using the pipette.
2. Take the pipette tip off the pipette, holding it close to top, and rinse out the inside three times with MQ water.
3. Replace tip back on pipette and rinse the outside (the lower part, that the gloves haven't touched) with MQ water, then flick dry
4. Finally, if the pipette is being used with acid, pipette to waste the same amount of the same acid that the pipette is going to be used for.

4 Weighing

Aim

To select enough of the freshest and most phenocryst free chips, from the subset already chosen from the crushing stage, to go forward for cleaning, dissolution and analysis, such that the mass of analyte is sufficient to make precise measurements.

Notes

Pb is likely to be the limiting element in terms of the amount of sample that needs to be dissolved in order to recover a measurable mass. Typical concentrations of Pb:Nd:Sr in basaltic whole rocks from Iceland might be ~0.5:8:200 ppm. For optimal results it is preferable to be running ~ **100 ng** Pb, therefore use the equation:

$$M_p = \frac{100 \times 10^{-3}}{[Pb]}, \quad (1)$$

to calculate the mass of sample that needs to be picked, M_p , such that it contains at least **100 ng** of Pb, given the concentration of Pb in the basalt, $[Pb]$, in ppm.

4.1 Procedure

1. Wipe down the inside of the weighing area, place a clean kimwipe beside the scales which will catch any material that misses the vials.
2. Static will cause the recorded mass on the scales to vary from the ‘true’ value. In order to avoid this, (1) fill a small beaker with MQ water and stand it in the back of the scales, (2) don’t wear gloves, (3) use a static gun, (4) try making repeat measurements.
3. Open the 15 ml Savillex vial which is to have sample added and close again, this adds static (which all subsequent measurements will have) and equilibrates vial atmosphere with room. Then weigh and record the vial mass.
4. Remove the vial from the balance and add the sample to it, preferably by pouring chips into the vial without touching them.
5. Re-weigh the vial, making sure that the added mass is $\geq$ the calculated mass of sample, M_p and record in table:

Sample number	Vial number	$M_{Vial+Lid}$	$M_{Vial+Lid+Sample}$	M_{Sample} $(= M_{Vial+Lid+Sample} - M_{Vial+Lid})$
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6. Clean tweezers/spatula (if used to add sample) and the weighing area surface between samples.

5 Sample Cleaning: Whole rock and glass chips

Aim

To remove loose altered material from the exterior and cavities of the chips.

5.1 Procedure

1. Add enough MQ water to vials such that the samples are covered. Be careful to keep the samples upright once they have had MQ water added.
2. Place vials in ultrasonic bath for **20** minutes (it will hold 8 samples). Only fill the ultrasonic bath with MQ water so far as to match the water level in the vials - do not fill up so that the water touches the vial lids.
3. On removing from ultrasonic bath pipette off supernatant, disposing of tip between samples to avoid cross-contamination.
4. Rinse samples a further five times by refilling with MQ water and pipetting off supernatant. Avoid pushing the chips into the bottom of the vial with the pipette tip, this will scratch the vial's surface.
5. Dry down: place on hot plate in drying box.
6. Once dry re-weigh the sample.

6 Leaching

Aim

To remove any foreign elemental contribution not structurally bound into the sample, i.e. alteration products, anthropogenic Pb or Sr from weathering or interaction with sea water, which would cause the measured isotope ratios to deviate from their mantle derived values.

Notes

The underlying assumption of leaching samples is that the foreign elemental contribution will be more readily mobilised than that bound into the basalts during their formation. Caution needs to be taken when leaching heterogeneous samples, those that consist of more than simply a sample mono-phase and contaminant phase. If the sample material being analysed is itself polyphase, for example phenocrysts and ground-mass, then one needs to be conscious that leaching will preferentially attack different phases, and the possible consequences of that for the proportion of Pb/Sr/Nd each phase ultimately contributes to the total sample Pb/Sr/Nd.

6.1 Leaching: Whole rock chips

6.1.1 Procedure

1. First tap vials to get all the grains to the bottom, static will be causing them to stick to the sides of the vial.
2. Add $\sim 1 \text{ ml } 6 \text{ N HCl}$ to the samples, or just enough so that they are covered. Swill round inside of vial to cover all grains.
3. Place the samples on a hotplate at 150°C for **1 hr**.
4. Remove from hotplate and allow to cool.
5. Pipette off leachate into micro-centrifuge bullet.
6. Add fresh batch of 6 N HCl to the samples, just enough so that they are covered. Swill round inside of vial to cover all grains.
7. Ultrasonicate vials for **20 min**.
8. Dry the outside of the vials and place back on hotplate at 150°C for **30 min**.
9. Remove from hotplate and allow to cool.
10. Pipette off leachate into same micro-centrifuge bullet.
11. Rinse each sample five times by adding MQ water and pipetting the supernatant to waste.
12. Allow the samples to dry down overnight on the hotplate at $\sim 40^\circ\text{C}$.
13. Reweigh the vial and sample, this constrains the mass lost to the leaching process.

6.2 Leaching: Glass chips

6.2.1 Procedure

1. First tap vials to get all the grains to the bottom, static will be causing them to stick to the sides of the vial.

2. Add $\sim 1 \text{ ml } 6 \text{ N HCl}$ to the samples, or just enough so that they are covered. Swill round inside of vial to cover all grains.
3. Ultrasonicate vials for **20 min.**
4. Dry the outside of the vials and place on hotplate at **150°C** for **30 min.**
5. Remove from hotplate and allow to cool.
6. Pipette off leachate into micro-centrifuge bullet.
7. Rinse each sample five times by adding MQ water and pipetting the supernatant to waste.
8. Allow the samples to dry down overnight on the hotplate at $\sim 40^{\circ}\text{C}$.
9. Reweigh the vial and sample, this constrains the mass lost to the leaching process.

7 Sample Dissolution: Whole rock and glass chips

Aim

Basalt samples need to be dissolved using hydrofluoric acid, to ensure complete digestion of all phases and thus that a true bulk sample chemistry is obtained. Samples by this stage will have undergone leaching in 6N D-HCl, in order to remove any surficial contaminant phases, but should be dry residues and grains in **15 ml** Savillex vials.

Calculating the volume of HF required to dissolve a sample:

HF reacts with the sample to produce silicon tetrafluoride, which will evaporate off on dry down. For this reaction to go to completion requires that there be four atoms of fluorine for every one atom of Si. We will first calculate the number of moles of SiO₂ present in the endmember case where our sample consists of pure quartz, and assume that an unusually large mass of sample has been added, 0.4 g.

$$m_{\text{SiO}_2} = 60.0843 \text{ g/mole},$$

$$M_{\text{sample}} = 0.4 \text{ g}.$$

Number of moles of SiO₂ in sample (assuming endmember case of pure quartz),

$$N_{\text{sample}}^{\text{SiO}_2} = M_{\text{sample}}/m_{\text{SiO}_2} = 0.006657.$$

Four atoms of F required to bond with every atom of Si, therefore number of moles of HF required,

$$N_{\text{HF}}^{\text{required}} = 4 * N_{\text{sample}}^{\text{SiO}_2} = 0.0266.$$

We use 40%HF, which has a molarity of 22.6 (moles/litre). We add 1.5ml of HF to each sample, therefore the number of moles of HF added,

$$N_{\text{HF}}^{\text{added}} = 1.5/1000 * 22.6 = 0.0339.$$

As $N_{\text{HF}}^{\text{added}} > N_{\text{HF}}^{\text{required}}$ for the most challenging scenario pure quartz, 1.5 ml HF should be more than adequate to dissolve any basaltic sample, which will have only around 50 wt% SiO₂.

7.1 Preparation

Learning about HF

- Attend the university HF safety course.
- Read the department guidelines for HF use: Appendix 3: Hydrofluoric acid

Informing others

- Arrange in advance for a department first aider to be present during the hours in which you are going to be using HF. The first aiders are Jason Day, Charlie Aldous and Steve Laurie. Ring them just before you open the HF and as soon as you have finished using it.
- Ensure that there is somebody nearby whilst you are using HF. They need to be able to call for assistance if there is an accident.

- Inform other lab users that you are going to be performing HF chemistry. There are warning signs that you should put up around the area in which you are working and any extraction-clean-box/fume cupboard that contains HF.

Setting up the lab area

- Do not sit down whilst performing HF work.
- Work in a fume cupboard, the HF will begin to evaporate as soon as it is exposed to the air.
- You should work in an area with a sink, if there is a spillage or you get any on you lots of water is going to be required for rinsing and cleaning affected surfaces.
- Perform all work with HF in plastic trays. Any spillage is thus contained and easily cleaned up.
- Have HF neutralising gel (calcium gluconate gel) nearby.
- Have box of Kimwipe tissues handy.
- Have a squeeze water bottle for cleaning pipette tips etc. before they are safely disposed of.
- Have a sealable plastic bag into which used, rinsed, equipment can be placed, which can then be safely put into the lab bin at the end of your work.
- Pour from the HF bottle into an intermediate size container, for example a **60 ml** Savillex beaker. Pipette from this smaller Savillex beaker into sample vials.

Personal Protective Equipment

- Wear protective glasses, with larger face shield over the top.
- A Tyvek suit and apron should be worn.
- Wear clogs.
- Depending on length of HF use, either wear two pairs of disposable gloves and remove immediately if any HF splashes onto them. Or if handling large quantities of HF (i.e. when pouring from the bottle into a smaller container), wear the thicker gauntlet type gloves. These go up above the elbow to offer more complete protection from splashes. Even in this case wear disposable gloves underneath.
- Test gloves before use by inflating and submerging the finger tips in water.
- With all gloves you use when handling HF, ensure the outer pair extend over the sleeves of your Tyvek suit.

7.2 Procedure

Add HF

1. Turn the hotplate on at **110°C** and place the graphite holder block on top.
2. Take vials and place them lined up on a tray inside a fume cupboard, they should contain dry sample.
3. Loosen the caps so that acid can be easily and quickly added.
4. First add **3 ml 16 N HNO₃** to each vial.

5. Pour from the HF beaker into the intermediate sized container the approximate amount of HF you need. It is best to pour too much than have to repeat this step.
6. Prime the pipette tip for use with HF by first drawing up **1.5 ml HF** and pipetting it into a waste beaker with **> 100 ml MQ water** in it.
7. Next add **1.5 ml 50% conc HF** to the samples, pipetting slowly and steadily into the vial. Avoid splashes by slow depression and release of the pipette button.
8. Tightly cap the vials after HF has been added to each.
9. Carefully transfer vials to digest on the hotplate at **110°C** for **24 hr** in the fume cupboard. Place the vials in the graphite blocks to apply a uniform heat.
10. Clean the work area, tray and all materials before they are disposed of.
11. After **24 hr** carefully check the samples to see if they have entirely dissolved. If there are vials with significant amounts of black material remaining, add a further **1 ml HF** to each vial (whether sample remaining or not).
12. After checking on the samples, leave to dissolve for another **24 hr**.

Dry down

13. **48 hr** after first adding HF, remove the vials from the hotplate and allow to cool.
14. Once cool, roll each vial to remove large droplets from the lid and carefully open each vial briefly in the fume cupboard to release any HF fumes.
15. Transfer the samples onto a hotplate in a dedicated extraction clean box, set at **70 °C**, to dry down. **Clearly label with HF hazard signs.**

Re-dissolve in HCl

16. Once the samples have dried completely, add **4 ml 6 N HCl** to each sample and place on a hotplate at **85°** for **~ 1 hr** to bring into solution.
17. After the samples are dissolved, take off the hotplate to cool.
18. When the samples have cooled place back on the hotplate to dry down. At this stage check the samples are digested and no dark residues remain, some solutions may appear cloudy due to the formation of fluoride salts.

8 5% Cuts

Aim

To preserve a fraction of the sample that can be run for concentrations. At this stage elemental fractionation should not have taken place.

8.1 Developments

Adding 11 ml of nitric to the samples still failed to fully dissolve the precipitate. The cut was taken regardless. A new method will have to be found for taking 5% cuts in samples that do not easily go into complete solution. Options include: using larger vials in order to be able to add more nitric; gently heating the samples, maybe to 40°C; Using a stronger acid, 6 N HNO₃ instead of 3 N?

8.2 Procedure

To make 5 ml of 6 N HNO₃ add 3.846 ml 3 N HNO₃ and 1.154 ml 16 N HNO₃ to a dried sample.

1. Add precisely **5 ml 6 N HNO₃** to the samples.
2. Leave to dissolve. Place on hotplate if necessary.
3. Check the samples are dissolved; the solution should be a clear, with no solid residue.
4. Pipette **0.25 ml** of each sample into a labelled **1.5 ml** microcentrifuge tube. Store the tubes in a labelled zip-seal bag.
5. Dry down the remaining sample overnight at **70°C**.

If the above procedure fails due to incomplete dissolution of the sample, first try adding additional nitric acid.

9 Pb Chemistry

Aim

To separate as pure a Pb cut as possible from the bulk sample, to go on to be run in the MC-ICP-MS for isotopic analysis.

9.1 Anti-contamination precautions

Pb results are highly sensitive to contamination, because of the low concentrations of Pb in basalts and the pervasive presence of Pb in man-made materials and the atmosphere. As a result extra precautions need to be taken to obtain high accuracy and high precision results:

- Perform the Pb chemistry first, before taking the sample through TRU spec and Ln spec.
- Clean all surfaces inside the clean box in which Pb chemistry is to be performed. Pay particular attention to overhanging surfaces that could release particulate matter down onto the columns.
- Do not reach over open vials or columns.
- Do not lean over a beaker to peer inside it.
- Wipe down all vials before opening them. Check that any fibres etc. that might be stuck to the surface are cleaned off before opening the vial.

9.2 Systematics

- Pb sticks to the resin when dissolved in HBr.
- Pb is mobilised in HCl.

Table 1: Summary table

1.	Dissolve samples and blank	1.2 ml	0.7 N HBr	
2.	Leave sample on hotplate			$\geq 1.5 \text{ h } 120^\circ \text{C}$
3.	Pipette sample into microcentrifuge tube			
4.	Centrifuge samples		10 minutes in 1.5 ml tubes	
5.	Rinse to waste	500 μl	MQ water	
6.	Rinse to waste	2.5 ml	6 N HCl	1 $\times$ 2.5 ml
7.	Flick acid from column to waste			In Pb box
8.	Rinse to waste	1 reservoir	MQ water	
9.	Prime the resin	1 ml	0.7 N HBr	
10.	Replace waste beaker with original sample vial			
11.	Load sample			
12.	Use squirt bottle to add MQ water to microcentrifuge tube and pipette to REE vial below			
13.	Elute to REE vial	400 μl	0.7 N HBr	$\times 3$
14.	Elute to REE vial	240 μl	2 N HCl	
15.	Flick acid from column			
16.	Replace REE vial with clean Pb vial			
17.	Elute the Pb to clean vials	1 ml	6 N HCl	$\times 2$
18.	Dry samples down overnight			Pb at 65°C

9.3 Procedure

This procedure will be repeated **twice**, to remove as much matrix from the Pb as possible. The resin used is **AG1-X8 100-200 mesh resin**.

1. Check that enough acid is available for all stages of the chemistry, it requires:
3.4 ml 0.7 M HBr / sample
4 ml 6 N HCl / sample
240 μ l 2 N HCl / sample
5 ml QD 16 N HNO₃ total
2. To make **100 ml 0.7 M HBr** add **7.8 ml 9 M HBr** (yellow stock solution stored in left-hand fume cupboard) to **92 ml MQ water** using measuring cylinders.

Pb column preparation

1. Clean column stand with MQ water and place in clean cabinet. For Pb chemistry the column racks with slots cut into them should be used.
2. Place waste cups underneath the column slots.
3. Take clean, dry column caps from appropriately labelled bag and place one over each column slot.
4. Pour the acid off the columns into the sink in the fume hood, with the water running. The columns are stored in dilute HNO₃ in a plastic container, which is on the hotplate in the fume hood.
5. Rinse columns in container a few times using MQ water from tank next to sink.
6. Taking the columns one by one from the container, check that the frit is in the right position (**1/3** of the way down) and that the column has only a small collar/no collar and thus will sit securely in the slotted column rack.
7. Clean the columns thoroughly with MQ water, using a squirt bottle to force water through the frit from both top and bottom. To avoid air bubbles getting trapped in the column squirt in MQ water from the bottom, quickly flip over and fill from top. Shake dry and repeat.
8. Fill the column with water such that no air bubbles are included. Place column in column stand and inject **AG1-X8** resin from the squirt bottle (stored in the Pb clean cabinet).
9. Let the resin settle onto the frit and the water drain through.
10. Once the water has drained through there should be resin sitting above the frit in a continuous column, with no air bubbles. The resin should extend to the rim at the base of the reservoir.
11. If there are air bubbles squirt MQ water into the column from its base, re-suspending the resin and driving out any bubbles. Place the column back in the stand to settle.
12. If there is not enough resin in the stem, re-suspend the resin by squirting MQ water up the stem and into the reservoir above. Add more resin to the reservoir and allow to settle.
13. If there is too much resin the column, slowly add water to the reservoir to re-suspend some of the resin. Pipette off the excess and return it to the resin bottle.

Re-dissolve samples

1. Take dried samples and add **1.2 ml 0.7 M HBr** to each.
2. Recap the vials and gently swirl the HBr over the inside of the vial.
3. Place on the hotplate at **120°C** for **1.5 hr**.

Clean and prepare the columns

1. Add **500 μ l MQwater** to drain through the columns.
2. Once the MQ water has dripped through, flick the remaining water in the column stem to waste.
3. Add **2.5 ml** of **6 N HCl** to each column, running the acid around the inside edge of the reservoir, and let it drip through. This scavenges any Pb in the reservoir and resin.
4. Flush away the HCl with a reservoir of MQ water and wait for it to drip through.
5. Once the MQ water has dripped through, flick the remaining water in the column stem to waste.
6. Prime the columns by adding **1 ml 0.7 M HBr** and letting it drain through.
7. Once the HBr has dripped through, gently tap the columns, flick away the acid from the column stems into a waste tub and then return to the stand.

FIRST PASS: Centrifuge samples

1. Place vials in ascending order in the clean cabinet. Label them 1–**n** in the lab book and assign vials in that order to the columns, these vials will be used to collect the REE cut.
2. Prepare a set of cleaned **15 ml** vials, also place in ascending order in the clean cabinet and assign to samples accordingly. These vials will collect the Pb cut.
3. Take cleaned microcentrifuge tubes, label the lids 1–**n**, record relation to samples in lab book and then place the tubes in front of the corresponding vials in the clean cabinet.
4. If it is possible to pour all the sample (solids and supernatant) directly into the microcentrifuge tubes then do this. Else...

Take **1000 μ l** pipette and a box of new tips, set dial to **600 μ l**. Draw some liquid from the vial into the pipette tip and squirt back into the vial, this stirs the sample up. Repeat to ensure that all the sample is in solution. Transfer all liquid and solids from the vials into the **1.5 ml** microcentrifuge tubes and close lids.

5. Centrifuge the samples in the mini centrifuge for **10 minutes** at **13000 rpm**. Make sure it is balanced before starting.
6. Once centrifuging has finished load the supernatant into the columns as soon as possible. It is important to avoid re-suspending any precipitate that has formed at the bottom of the microcentrifuge tube.

FIRST PASS: Load the samples into the columns

1. Replace the original vials beneath the columns to collect the REE cut.
2. Take **1000 μ l** pipette set to **700 μ l** and rinse it with MQ water and once with HBr.
3. Draw **0.7 ml** of supernatant from the microcentrifuge tube into the tip, avoiding the precipitate, and add it to the corresponding column.
 - To prevent entrainment of precipitate, tilt the microcentrifuge tube towards yourself so that the precipitate (which will be piled up on one side) is lying as flat as possible. Then pipette slowly from the top down, taking small amounts of supernatant at a time.
 - Repeating this procedure allows nearly all the supernatant to be extracted, and when finally the precipitate is disturbed only a small fraction of the supernatant is lost.
4. Add some MQ water to the microcentrifuge tube and scratch its walls and base with the pipette tip to get as much of the precipitate as possible into suspension.

5. Pipette this fluid and precipitate into the REE beaker below the columns.
6. Dispose of the microcentrifuge tube and pipette tip.

SECOND PASS: Load the samples into the columns

1. Replace the original vials beneath the columns to collect the REE cut.
2. Carefully pour the Pb cut from the first pass vials into the column reservoir.
3. Rinse the old Pb vials three times in MQ water then fume on a hotplate at 85°C with 6 N HCl.

Collect the REEs

1. Once the sample has dripped through, add **400 μ l 0.7 M HBr** and allow to drain into the original vials. Repeat three times.
2. Add **240 μ l 2 N HCl** to the columns and drain through, collecting in the same vials beneath the columns. After this only the Pb should be left in the columns.
3. Gently tap the columns and then remove the vials from under them.
4. Dry down this cut on the hotplate overnight at **65°C**.
5. Flick away the remaining acid in the column stem.

Elute the Pb

1. **SECOND PASS:** Pour hot HCl from the vials into the fume cupboard sink.
2. Place the assigned Pb vials beneath the appropriate columns.
3. Add **1 ml 6 N HCl** to the columns and collect in the new vials.
4. Once this acid has dripped through add a second **1 ml 6 N HCl** to the columns.
5. Once all the acid has dripped through, tap the column to remove any drips left on the stem tip.
6. Dry down the Pb cut overnight on the hotplate at **65°C**.
7. **SECOND PASS:** After the Pb cut has dried, add a few drops of 16N QD HNO₃ to each sample. This is in an attempt to break down any organics leached from the resin.

Clean-up

1. Clean the columns.
 - Take the container in which the columns were stored and fill it half full with MQ water.
 - Take the columns one by one and inject MQ water into the stem and reservoir.
 - Repeat filling and shaking out of column until all the resin is removed.
 - With the stem free of air bubbles, fill the reservoir with MQ water and place into container.
 - Cap the container and take to fume hood, now add **~ 5 ml 16 N QD HNO₃** to the water to create a dilute acid.
 - Replace cap and place on hotplate at **85°C**.
2. Clean column stands and exposed work surfaces with MQ water.
3. Rinse column caps three times with MQ water and place in drying cupboard.
4. Thoroughly clean the inside and outside of the Pb cabinet.

Repeat

Perform this procedure a total of two times, in order to purify the Pb cut.

10 TRU Spec Chemistry

Aim

To separate out the REE.

10.1 Systematics

- Nd will stick to the resin when in HNO_3 .
- REE are mobilised in HCl .

Table 2: Summary table

1.	Wash column	$3 \times 1 \text{ ml}$	1 N HCl	Removes contaminant REE
1.	Purge HBr from sample	few drops	16 N HNO_3	
2.	Dissolve samples and blank	1 ml	1 N HNO_3	
3.	Flick acid from column			Avoid capillary action
4.	Prime column	1 ml	1 N HNO_3	Charges the resin
5.	Centrifuge sample			10 minutes at 13000 rpm
6.	Flick acid from column			Avoid capillary action
7.	Load sample			Pipette avoiding solids
8.	Wash to non-REE (Sr) beaker	$2 \times 500 \mu\text{l}$	1 N HNO_3	Collect Sr and other cations
9.	Flick acid from column			Avoid capillary action
10.	Elute to REE beaker	$3 \times 1 \text{ ml}$	1 N HCl	Collect REE
11.	Dry non-REE (Sr) cut at 55°C			
12.	Dry the REE cut on the hotplate at 45°C . Do not fully dry to a solid			

10.2 Procedure

This procedure will be performed once, to separate the REE from the cut which will go on through Sr chemistry. The resin used is **Eichrom TRU resin TR-B25-A** and is stored in a 30ml vial in the clean cabinet.

Check that enough acid is available for all stages of the chemistry, it requires:

A few drops 16 N HNO_3 / sample

3 ml 1 N HNO_3 / sample

6 ml 1 N HCl / sample

Preparation of Eichrom TRU resin TR-B25-A

This step takes ~ 1 hour, so prepare new resin the day before the TRU Spec chemistry is to be carried out.

1. Put dry Eichrom TRU resin TR-B25-A into the dedicated TRU resin Savillex vial.
2. Wash with 1 N HNO_3 .
3. Allow to fully settle and pipette off all floating resin.
4. Wash with MQ water, allow to settle and pipette off floating resin.
5. Repeat water wash until no floating resin is present (5-6 times).

Purge samples of HBr

Note: Come in early and perform this step first, the sample needs to dry again before it is picked up in 1 N HNO₃.

1. Clean the outside of the sample vials, removing any HBr drips.
2. Take samples and place in fume cupboard.
3. Pour a small amount (~ 1 ml) of QD HNO₃ into a clean vial.
4. Using the 1000 μ l pipette, add a few drops of **QD HNO₃** to each sample.
5. Cap the vials and transfer them to a drying cabinet to dry down.

Prepare TRU Spec columns

1. Clean column stand with MQ water.
2. Place waste cups underneath the column slots.
3. Take clean, dry column caps from appropriately labelled bag and place one over each column slot.
4. Pour the acid off the columns into the sink in the fume hood, with the water running. The columns are stored in dilute HNO₃ in a plastic container, which is on the hotplate in the fume hood.
5. Rinse columns in container a few times using MQ water from tank next to sink.
6. Taking the columns one by one from the container, check that the frit is in the right position (**1/3** of the way down) and that the column has only a small collar/no collar and thus will sit securely in the slotted column rack.
7. Clean the columns thoroughly with MQ water, using a squirt bottle to force water through the frit from both top and bottom. To avoid air bubbles getting trapped in the column squirt in MQ water from the bottom, quickly flip over and fill from top. Shake dry and repeat.
8. Fill the column with water such that no air bubbles are included.
9. Take 1000 μ l pipette and set it to 350 μ l. While there is still water in the column's reservoir inject the TRU Spec resin, entraining as little water as possible from the vial.
10. Once all columns have had resin added move the rack to the clean cabinet.
11. Let the resin settle onto the frit and the water drain through.
12. Once the water has drained through there should be resin sitting above the frit in a continuous column, with no air bubbles. The resin should extend to the rim at the base of the reservoir.
13. If there are air bubbles squirt MQ water into the column from its base, re-suspending the resin and driving out any bubbles. Place the column back in the stand to settle.
14. If there is not enough resin in the stem, re-suspend the resin by squirting MQ water up the stem and into the reservoir above. Add more resin to the reservoir and allow to settle.
15. If there is too much resin the column, slowly add water to the reservoir to re-suspend some of the resin. Pipette off the excess and return it to the resin vial.

Re-dissolve the samples

1. Add **1 ml 1 N HNO₃** to each sample.
2. Place the cap back on, swirl gently.
3. Leave to dissolve for 1 hour on a hotplate at **55°C**.

Clean and prepare the columns

1. Add **1 ml 1 N QD HCl** to each column and let it drip through to waste. **Perform this step 3 times.**
2. Flick away the acid from the column stems into a waste tub and return them to their stand.
3. Prime the columns by adding **1 ml 1 N QD HNO₃**, allow it to drip to waste.
4. With the acid drained through the resin, gently tap the columns to remove drops from the stem.
5. Flick any remaining acid in the column's stem into a waste tub and return them to the stand.

Centrifuge samples

1. Place vials in ascending order in the clean cabinet. Label them 1–**n** in the lab book and assign vials in that order to the columns, these vials will be used to collect the non-REE cut (i.e. that which goes on to Sr chemistry).
2. Prepare a set of cleaned **15 ml** vials, also place in ascending order in the clean cabinet and assign to samples accordingly. These vials will collect the REE cut.
3. Take cleaned microcentrifuge tubes, label the lids 1–**n**, record relation to samples in lab book and then place the tubes in front of the corresponding vials in the clean cabinet.
4. Transfer samples to microcentrifuge tubes.
 - Take **1000 µl** pipette and a box of new tips, set dial to **600 µl**. Draw some liquid from the vial into the pipette tip and squirt back into the vial, this stirs the sample up. Repeat to ensure that all the sample is in solution. Transfer all liquid and solids from the vial into the **1.5 ml** microcentrifuge tube and close lid.
 - Now place the microcentrifuge tube on the tube rack.
 - Repeat for each sample using a new pipette tip each time.
5. Centrifuge the samples in the mini centrifuge for **10 minutes** at **13000 rpm**. Make sure it is balanced before starting.
6. Once centrifuging has finished load the supernatant into the columns as soon as possible. It is important to avoid re-suspending any precipitate that has formed at the bottom of the microcentrifuge tube.

Load the samples into columns

1. Place the original vials beneath the columns, these will collect the non-REE cut.
2. Take **1000 µl** pipette set to **700 µl** and rinse it with MQ water.
3. Draw **0.7 ml** of supernatant from the microcentrifuge tube into the tip, avoiding the precipitate, and add it to the corresponding column.

- To prevent entrainment of precipitate, tilt the microcentrifuge tube towards yourself so that the precipitate (which will be piled up on one side) is lying as flat as possible. Then pipette slowly from the top down, taking small amounts of supernatant at a time.
 - Repeating this procedure allows nearly all the supernatant to be extracted, and when finally the precipitate is disturbed only a small fraction of the supernatant is lost.
4. Add some MQ water to the microcentrifuge bullet and scratch its walls and base with the pipette tip to get as much of the precipitate as possible into suspension.
 5. Pipette this fluid and precipitate into the REE beaker below the columns.
 6. Dispose of the microcentrifuge tube and pipette tip.

Collect the non-REE cut

1. Once the sample has dripped through add **500 μ l 1 N QD HNO₃** and allow to drain into the original vials. **Perform this step twice.**
2. Tap the columns to remove drips left on the stem.
3.
 - All but the REE should now have been flushed from the TRU Spec resin and collected in the original vials. Remove the vials from beneath the columns and dry down this cut at **55°C**.
 - Following dry down of this cut, pick it back up in 1.5 ml 6 N HCl, leave on the hotplate at 85°C for at least an hour and then dry down overnight. The sample needs to be a chloride salt before it is picked up for Sr chemistry.
4. Flick acid remaining in the column stem into a waste tub.

Elute the REE cut

1. Place the assigned REE vials beneath the appropriate columns.
2. Add **1 ml 1 N QD HCl** to the columns and collect in the new vials. **Perform this step 3 times.**
3. All the REE should now have been flushed from the resin. Dry down this cut overnight at **40°C**. Do not fully dry to solid as it will then be hard to dissolve for LN Spec. This will take **~ 40 hr**. The samples should end up as 1 mm sized gel-like transparent beads.

Clean up

1. Clean the columns.
 - Take the container in which the columns were stored and fill it half full with MQ water.
 - Take the columns one by one and inject MQ water into the stem and reservoir.
 - Repeat filling and shaking out of column until all the resin is removed.
 - With the stem free of air bubbles, fill the reservoir with MQ water and place into container.
 - Cap the container and take to fume hood, now add **~ 5 ml 16 N QD HNO₃** to the water to create a dilute acid.
 - Replace cap and place on hotplate at **80°C**.
2. Clean column stands and exposed work surfaces with MQ water.
3. Rinse column caps three times with MQ water and place in drying cupboard.
4. Thoroughly clean the inside and outside of the Pb cabinet.

11 Ln Spec Chemistry

Aim

To separate out Nd from the other REE.

11.1 Systematics

- Nd is both washed into the resin and eluted with **0.3 N QD HCl**.
- **6 N QD HCl** is used to purge the columns.

Table 3: Summary table

1.	Dissolve the samples	100 μl	0.3 N QD HCl	
2.	Unwrap columns			Be careful to preserve their order
3.	Clean columns	4 ml	6 N QD HCl	Remove contaminants
4.	Equilibrate columns	1 ml $\times$ 2	0.3 N QD HCl	Drip around the edges to clean
5.	Load sample	100 μl	0.3 N QD HCl	
6.	Rinse vial and load	100 μl	0.3 N QD HCl	Ensure all cations get to column
7.	Clean beakers		MQ	Rinse, scrub, fume in acid
8a.	Wash to waste beaker	100 μl	0.3 N QD HCl	Remove unwanted cations
8b.	Wash to waste beaker	200 μl	0.3 N QD HCl	Remove unwanted cations
8c.	Wash to waste beaker	500 μl	0.3 N QD HCl	Remove unwanted cations
9'.	Wash to waste beaker	4 ml col 1 and 5	0.3 N QD HCl	Remove unwanted cations
9''.	Wash to waste beaker	5 ml col 14 and 21	0.3 N QD HCl	Remove unwanted cations
9'''.	Wash to waste beaker	4.5 ml other cols	0.3 N QD HCl	Remove unwanted cations
10.	Elute to centrifuge tube	1 ml	0.3 N QD HCl	Collect in case of calibration error
11.	Elute to cleaned beaker	2.5 ml	0.3 N QD HCl	Collect Nd
12.	Elute to centrifuge tube	0.5 ml	6 N QD HCl	Collect in case of calibration error
13.	Wash waste to beaker	2.5 ml	6 N QD HCl	Cleans remnant cations
14.	Equilibrate and store	1 ml	0.3 N QD HCl	Fill columns and store in Teflon
15.	Slowly dry down Nd cut on hotplate at 45°C			

11.2 Procedure

Ln columns are used repeatedly and the elution curves are pre-calibrated.

Check that enough acid is available for all stages of the procedure, it requires at most per column:

12.6 ml 0.3 N QD HCl

7 ml 6 N QD HCl

Re-dissolve the samples

- Prior to dissolution samples should be small (~ 1 mm), gel-like, transparent, pale brownish beads on the bottom of the vials. Do not dry them down completely - dry samples are difficult to dissolve in the **0.3 M QD HCl**.
1. Add **100 μ l 0.3 M QD HCl** to each vial using the 1000 μ l pipette. Ensure that the acid is added directly onto the sample.

2. Leave the sample to dissolve for **1 hr**.

Prepare the columns

1. Clean the Ln column stands with MQ water and place into the clean cabinet.
2. Wipe clean the outside of the column reservoirs.
3. Unwrap the columns and place them in ascending order into the column stands.
4. Place clean waste cups beneath each of the columns.

Clean the columns

1. Add **4 ml 6 M QD HCl** to each column.
 - Add the acid drop by drop around the inside edge of the reservoir to wash out any previous sample.
 - Immediately after adding the acid place the cap on the column.
 - This amount of acid takes ~ 60 minutes to trickle through.

Prime the columns

1. Add **1 ml 0.3 M HCl** to each column.
 - Add the acid drop by drop around the inside edge of the reservoir to wash out the 6 M HCl.
2. After the first 1 ml 0.3 M HCl has dripped through the columns, add a second **1 ml**. 1 ml takes ~ 15 minutes to trickle through.

Load samples into the columns

1. Take the 200 μl pipette and set dial to 120 μl .
2. Place the vials containing the REE cut in ascending order and assign them to the columns.
3. Take the caps off all the columns and place them on the column stand beside the column reservoirs.
4. Load the samples into the columns one by one.
 - Draw some liquid from the vial containing the sample into the pipette tip, avoiding flakes, and squirt it back onto the undissolved remnants of the sample.
 - Repeat this until all the sample is in solution.
 - Draw as much of the liquid from the vial into the tip as possible - leave only solids behind. Ensure that *no solids* are drawn into, or stick onto, the tip of the pipette: these will clog up both the resin and the tip.
 - Add the samples drop by drop onto the resin.
 - Immediately after adding the sample to the column place the cap back on.
 - Place the vial in front of the respective column and place the pipette tip into the vial.
5. Add **100 μl 0.3 M QD HCl** to each 15 ml vial.
6. Load the remaining sample from each vile into the columns one by one.
 - Take **200 μl** pipette with dial set to **120 μl** .

- Scratch the bottom of the vial with the tip if there is any undissolved sample stuck to it, also try spraying sample at any remaining gels or solids to try and disturb them.
 - Once the entire sample is dissolved, draw the liquid into the tip and add the last drops to the corresponding column.
 - Place the cap back on the column.
7. Allow the 100 μ l 0.3 M QD HCl to trickle through the resin.

Clean the Teflon vials

1. Rinse vial and cap three times in MQ water.
2. Scrub the inside of the vial thoroughly with clean wet tissue paper.
3. Rinse the vial again three times and re-cap.
4. Take the vials to the fume cupboard.
5. Add $\sim$ 1 ml 6 N HCl to each vial using the squirt bottle and re-cap.
6. Place the vials into the graphite heating block on the hotplate at **85°C** for at least **1 hr**.

Add 800 μ l 0.3 M QD HCl to the columns in three steps:

- This serves to wash the sample into the resin and unwanted cations to waste.
1. Add **100 μ l 0.3 M QD HCl** to the columns and allow to trickle through.
 2. Add **200 μ l 0.3 M QD HCl** to the columns and allow to trickle through.
 3. Add **500 μ l 0.3 M QD HCl** to the columns and allow to trickle through.

Add 4 or 4.5 ml 0.3 M QD HCl to the columns:

- This serves to wash the samples through the resin and unwanted cations to waste.
1. Add **4 ml 0.3 M QD HCl** to columns *1 and 5*.
 2. Add **5 ml 0.3 M QD HCl** to columns *14 and 21*.
 3. Add **4.5 ml 0.3 M QD HCl** to *all other columns*.
 4. **4.5 ml** takes $\sim$ 1 h to trickle through the resin.

Collect pre-Nd cut

1. Label 15 ml centrifuge tubes by column number.
2. Once the 0.3 M QD HCl has trickled through the resin gently tap the columns to remove the last drops of acid into the waste cups.
3. Take the waste cups from under the columns and pour the acid into the sink. Rinse the waste cups with MQ water.
4. Place the 15 ml centrifuge tubes beneath the corresponding columns.
5. Use the 1000 μ l pipette to add **1 ml 0.3 M QD HCl** to the columns and collect in the centrifuge tubes. At this stage Nd starts coming off the resin.
6. Once the acid has dripped through the resin tap the columns to remove the last droplets of acid.
7. Remove centrifuge tubes from underneath columns.

Replace centrifuge tubes with clean vials

1. In the fume hood, remove vials from hotplate and roll acid around the insides, collecting all the droplets.
2. Pour acid into the fume cupboard sink with acid running.
3. Replace cap on vial, remove the vials from the fume hood and rinse three times with MQ water.
4. Place upturned waste beakers beneath each of the columns.
5. Stand the vials beneath their respective columns, on top of the waste beakers.

Elute the Nd to vials

1. Add **2.5 ml 0.3 M QD HCl** to columns *1 to 10*; add **3.0 ml 0.3 M QD HCl** to columns 11 to 24. Elute to the original vials.
2. Once the acid has trickled through the resin gently tap the columns to remove remaining drops of acid.
3. Dry down the samples on the hotplate at 45°C overnight.

Collect the post-Nd cut

- This Flushes remaining Nd from the columns and then washes them.
1. Place the centrifuge tubes back underneath their respective columns.
 2. Add **3 ml 6 M QD HCl** to each column.
 3. Collect the first **0.5 ml** in the centrifuge tubes, then remove them and re-cap.
 4. Allow the remaining 2.5 ml to drain into the waste cups.

Re-equilibrate the columns

- This serves to re-equilibrate the columns at a concentration of 0.3 M after having been washed at 6 M.
1. Add **1 ml 0.3 M QD HCl** to the columns.
 2. Allow most of the 1 ml 0.3 M QD HCl to trickle through the resin.

Wrap columns and clean up

1. Cut three square pieces of parafilm.
2. Before the 1 ml 0.3 M QD HCl totally drains from the column reservoirs, pull the caps tight onto the columns.
3. Remove the columns from the stand and place in a test tube with clean **0.3 M QD HCl**.
4. Wrap parafilm around the top of the test tube and the base of the column reservoir so that it holds them firmly together and place back in test tube rack.
5. Pour acid from waste cups and clean with MQ water.
6. Clean column stands and all work surfaces with MQ water.

12 Sr Chemistry: Cation II columns

Aim

To separate Sr from other cations for running on the TIMS, using cation II columns.

12.1 Systematics

- Sr is both washed into the resin and eluted with HCl.
- **6 N QD HCl** is used to purge the columns.

Table 4: **Summary table**

Table 1: Summary table			
1.	Dissolve the samples	400 μ l	1 N QD HCl
2.	Equilibrate columns	6 ml	1 N QD HCl
3.	Load sample	400 μ l	1 N QD HCl
4.	Wash sample into resin	100 μ l $\times$ 2	3 N QD HCl
5.	Elute non-Sr cations to waste	8.5 ml	3 N QD HCl
6.	Collect Sr	4 ml	3 N QD HCl
7.	Rinse column reservoir	2 ml $\times$ 2	6 N QD HCl
8.	Purge column	30.5 ml	6 N QD HCl
9.	Dry down Sr cut	Place in evaporating chambers overnight	

Use new beakers

12.2 Procedure

Sr columns are used repeatedly for a given sample set.

Check that enough acid is available for all stages of the procedure, it requires:

6.9 ml 1 N QD HCl

12.7 ml 3 N QD HCl

34.5 ml 6 N QD HCl

Prepare the resin

The resin used for Sr chemistry is , and is stored in a large tub beneath the clean cabinet.

1. Using the long scoop, transfer three scoops of resin into the large Savillex vial and add MQ water.
2. Rinse five times with MQ water, each time pouring off the supernatant to remove the fine fraction. Rotate the vial as you are pouring to best remove the foam of fines.
3. Once the supernatant is clear the resin is ready for use.

Make the columns

This step takes one day because of the large volume of acid left to drain through the columns.

1. Clean all the interior and exterior surfaces of the clean cabinet.

2. Clean the column stand and place inside the clean cabinet.
3. Remove any existing resin from the columns. Do this by turning the columns upside down and using the thick necked MQ dispenser to force water into the column through the stem. Discard the cotton wool frit.
4. Mark on the column stems the height to which they should be filled with resin, using a ruler and permanent marker.
5. Place the columns in the column stand, with clean waste beakers underneath.
6. Put a frit into each column:
 - Take the ball of cotton wool and pinch off a small amount, dropping a piece into each column's reservoir.
 - Use the glass rod to gently push the cotton wool to the bottom of each column's stem.
 - Flush through with a squirt of 6 N QD HCl.
7. Pipette the resin from large vial it is stored in into the columns: 2 ml of resin will leave most columns containing close to the right amount.
8. Swill around the inside of the column reservoir with ~ 2 ml 6 N QD HCl. Also rinse the bottom of the column stem with a small amount of 6 N QD HCl.
9. Repeat rinsing the column reservoir by squirting ~ 2 ml 6 N QD HCl around its inside edges.
10. Swill around the reservoir with 6 N QD HCl, then pour in 30 ml QD HCl.
11. Place parafilm over the top of the column and leave to drain through overnight.

Re-dissolve the samples

1. Add 0.4 ml 1 N QD HCl to each sample. Agitate the vial to ensure it all goes into solution.
2. If some sample remains undissolved, add more 1 N QD HCl and only load 0.4 ml onto the columns.

Equilibrate the columns

1. place clean waster beakers beneath the columns.
2. Add 6 ml 1 N QD HCl to each column, by first pipetting in 0.5 ml and then pour in the remainder from a measuring cylinder. Wait for this to drip through.

Centrifuge the samples

1. Place vials in ascending order in the clean cabinet. Label them 1–n in the lab book and assign the samples in that order to the columns.
2. Prepare a set of cleaned beakers, also place in ascending order in the clean cabinet and assign to samples accordingly. These beakers will collect the Sr cut.
3. Take cleaned microcentrifuge tubes, label the lids 1–n, record relation to samples in lab book and then place the tubes in front of the corresponding vials in the clean cabinet.
4. Transfer samples to microcentrifuge tubes.
 - Take 1000 μ l pipette and a box of new tips, set dial to 400 μ l. Draw some liquid from the vial into the pipette tip and squirt back into the vial, this stirs the sample up. Repeat to ensure that all the sample is in solution. Transfer all liquid and solids from the vial into the 1.5 ml microcentrifuge tube and close lid.

- Now place the microcentrifuge tube on the tube rack.
 - Repeat for each sample using a new pipette tip each time.
5. Centrifuge the samples in the mini centrifuge for **10 minutes** at **13000 rpm**. Make sure it is balanced before starting.
 6. Once centrifuging has finished load the supernatant into the columns as soon as possible. It is important to avoid re-suspending any precipitate that has formed at the bottom of the microcentrifuge tube.

Load the samples onto the columns

1. Take **1000 μ l** pipette set to **400 μ l** and rinse it with MQ water and then **1 N QD HCl**.
2. Draw **0.4 ml** of supernatant from the microcentrifuge tube into the tip, avoiding the precipitate, and add it to the corresponding column.
 - To prevent entrainment of precipitate, tilt the microcentrifuge tube towards yourself so that the precipitate (which will be piled up on one side) is lying as flat as possible. Then pipette slowly from the top down, taking small amounts of supernatant at a time.
 - Repeating this procedure allows nearly all the supernatant to be extracted, and when finally the precipitate is disturbed only a small fraction of the supernatant is lost.
3. Dispose of the pipette tip. If the sample was picked up in $> 0.4 \mu\text{l}$ HNO_3 then store the microcentrifuge tube containing this remaining sample, otherwise dispose of it.

Wash sample into resin

1. Pipette **0.1 ml 3 N QD HCl** into the columns, swilling around the base of the reservoir to ensure all sample reaches the resin. Wait for this to drip through.
2. Pipette a second **0.1 ml 3 N QD HCl** into the columns, swilling around the base of the reservoir to ensure all sample reaches the resin. Wait for this to drip through.

Elute non-Sr cations to waste

1. Add **8.5 ml 3 N QD HCl** to each column, first pipette in 0.5 ml and then pour the remainder from a measuring cylinder.

Collect Sr cut

1. Place Sr beakers beneath columns, standing on their lids and on blocks if necessary to bring them up to the height of the column tips. Be careful not to place the tip of the column too far into the beaker, else it will contact the sample when the vial is full.
2. Add **4 ml 3 N HCl** to columns. Use a pipette to add the first 0.5 ml and pour the remainder from a measuring cylinder.
3. Whilst this is draining through clean the area in which the samples are going to be dried down. First, wipe around the inside of the fume cupboard, then wipe the outsides and insides of each of the evaporating chambers and the bases on which they stand.
4. Once the acid has dripped through, remove the Sr beakers and place them under the evaporators to dry down overnight.

Purge the columns of cations

1. Place the waste beakers back beneath the columns.
2. Swill around the inside of the column reservoir with $\sim 2 \text{ ml } 6 \text{ N QD HCl}$. Also rinse the bottom of the column stem with a small amount of 6 N QD HCl .
3. Swill around the inside of the column reservoir with $\sim 2 \text{ ml } 6 \text{ N QD HCl}$.
4. Swill around the reservoir with 6 N QD HCl , then pour in 30 ml QD HCl .
5. Place parafilm over the top of the column and leave to drain through overnight.

Clean up

1. Wipe the inside of the clean cabinet down.
2. Wipe the blocks clean.

13 Spiking samples

Spiking of samples is performed during ‘isotope dilution’, in which a known amount of spike of a known isotopic composition is added to a sample (of measured composition) and the isotope ratio of the mixture analysed. The unknown in the mixing equation, the amount of analyte in the original sample, can then be solved for.

In isotopic studies, isotope dilution is useful for determining the amount of analyte in the blank. It is this use for which a method is provided.

13.1 Spiking a blank

1. Add **1 ml 2% HNO₃** to the blank vial and leave for **1 hr**.
2. In the weighing room, use the static gun to remove static from the spike beaker. To reduce static do not wear gloves.
3. Weigh the spike beaker without its parafilm wrapping. Repeat static removal and weighing to obtain an average weight for the spike beaker.
4. Use the static gun to remove static from both the blank vial and spike beaker.
5. Add a single drop of spike to the blank vial, ensuring that all spike leaving the spike beaker goes into the blank vial.
6. Use the static gun to remove static from the spike beaker and re-weigh. Repeat to obtain an average weight for the spike beaker.

Equation (2) below can be used to calculate the number of moles of analyte in the blank, where M_N is the number of moles of analyte element in blank, M_S is the number of moles of analyte element in the standard, A_S and A_N are the atomic fraction of the spike element in the spike and naturally occurring element (assumed/measured composition of contaminant phase), B_S and B_N are the atomic fractions of the reference isotope in the spike and natural element and R_M is the isotopic ratio measured from the spiked mixture (spike isotope/reference isotope).

$$M_N = M_S \frac{A_S - R_M B_S}{R_M B_N - A_N} \quad (2)$$

13.2 Pb example

When measuring a Pb blank, ^{208}Pb is the reference isotope, ^{206}Pb is the spike isotope enriched in the NBS 983 standard, and the 983 standard is prepared at 0.99 ppm. Broken Hill galena is taken as the assumed composition of contaminant Pb.

14 Running Samples on the Nu Plasma

14.1 Operating the Nu Plasma

Turning on the Nu

1. Turn on Argon supply to mass spec. Turn both knobs on far wall 90° counter-clockwise.
2. In the Nu software on the computer, check that valve 1 is green, i.e. open. This means that argon is able to reach the mass spec.
3. Turn on the nebulizer, the on-switch is at the back left-hand side of the nebulizer (as viewed from the front). Wait for at least 40 minutes for the nebulizer to warm up.
4. After 40 minutes light the torch on the Nu. To do this:
 - Turn the gas pressure on the nebulizer down to below 10 psi.
 - Turn the big chiller on (check that it has enough MQ water, if not top it up).
 - Press the green start button on the software window.
5. After 5 minutes increase the nebulizer pressure to run conditions (> 30 psi).
6. Go to Setup:Quad.values and select the element that is going to be analysed from the picture of the periodic table.

Focusing the Nu

The strategy for focusing the Nu should be to start with the most sensitive controls and move to the less sensitive ones, then iterate. The purpose is to maximise the beam intensity reaching the collector (i.e. the sensitivity), whilst also trying to ensure that the beam voltage remains relatively constant (i.e. the stability).

1. First make up a standard at the concentration the samples are going to be run at during the batch run, and have the mass spec analyse this standard.
2. Bring up the magnet scan window and adjust the scale so the beam you are focusing on is prominent (for Pb focus on H4, 208)
3. First vary the three settings on the Nebulizer. ‘Gas pressure’, ‘Hot gas flow’ and ‘Membrane gas flow’. Nebulizer normal operating conditions (from user manual):
 - Gas pressure (First dial): 30–40 psi.
 - Hot gas flow (Second dial): $0.15\text{--}0.3\text{ Lmin}^{-1}$.
 - Membrane gas flow (Third dial): $3\text{--}4.5\text{ Lmin}^{-1}$.
4. Next adjust the position of the torch in the plasma control box.
 - Back/Forward moves the torch out of or into the page (with respect to on-screen picture).
 - Up/Down moves the torch up or down on the on-screen picture.
 - In/Out moves the torch right or left in the on-screen picture.
5. Now move to the Deflection and HT supply window. The voltages in HT and source tab should be altered in the physical order the plates appear in the machine, from closest to the torch forwards. The order is thus: HV1, HV2, Source H1, Source V1, HV3, Source H2, HV6, Transfer V2, Transfer H1, HV5, Transfer V1. There is also a schematic of this in the NU user manual.
6. Now, iterate the above steps until the machine is fully focused.

Peak centering

The zoom lens and quadrupole magnets act in conjunction to get the beams of different mass into the cups, however, the beams' differing masses mean that the beams are not able to all be placed completely centrally in each cup. Although, all the beams can be made to be almost in the centre of their respective cups. The problem that having beams off-centre poses is that if, in fluctuating its position, less of a particular beam strikes its cup then the ratio recorded between it and another beam's voltage will be affected. To avoid this, the beams need to be centred prior to analysis.

1. Open up the magnet scan dialogue.
2. Select two beams to draw which cover the range of isotopes being studied.
3. Adjust the voltage scale on the y-axis until the traces of the beams on the graph overlap.
4. Next perform a magnet scan from half a mass unit below the atomic masses in the boxes, to half a mass unit above. The masses in these boxes are those of the axial, so mentally adjust this figure by one for each increment the cups under consideration are away from the axial.
5. Start the magnet scan, the beams should flat-line and then pick up as the magnet scans across the unit mass (e.g. 204).
6. From the trace it should be clear if the traces are overlapping, expect some asymmetry, but too much and the beam positions probably need slight adjustment.
7. To adjust the beams positions so they are as centred as possible for all beams, click the optimise button in the right of the magnet scan window.
8. After optimising the beam positions, stop the scan and drag the vertical bar (using the right mouse button) to the centre of the peak and click 'set magnet'. This sets the central position for all the beams.

14.1.1 Testing blank/background

Testing the blank for any acid/MQ solution is done by placing the autosampler into the test solution, and then once the beam has stabilised, comparing the voltage with and without the line of sight valve (LOS) closed. Example backgrounds/blanks are reported in Table 5.

Table 5: Backgrounds measured on 06-11-2011.

Input	Voltage obtained on H4, with 208 in this cup (V)
2 % HNO ₃	$< -5 \times 10^{-3}$
MQ	-5.5×10^{-3}
Air	-5.8×10^{-3}
LOS closed	-6.4×10^{-3}

Shutting down the Nu Plasma

1. Ensure that washouts have been run, at least 15 minutes in fluids (wash 3) followed by at least that long in air (wash 1).
2. Click the red stop button on the plasma control window.
3. Turn off the nebulizer using the switch on its rear.
4. Close off the supply of argon, both knobs on the far wall need to be rotated clockwise 90°.
5. Turn off the big chiller at the socket, which is on the wall above the bench in the entry way.

14.2 Cleaning apparatus in the Nu lab

The Nu lab is dirty compared to the lab in which the samples have been prepared and purified. Before doing any chemistry in the Nu lab ensure the clean box and all the surfaces which are going to be used have been thoroughly cleaned. Check that there is fresh MQ water and that there is sufficient 2% HNO_3 .

Sample tubes

Rinse the sample tubes three times with MQ water, pouring to waste. Flick the sample tube dry afterwards. Rinse once with 2% HNO_3 , flicking the tube dry afterwards.

Pipette tips

Clean pipette tips by drawing the required amount of 2% HNO_3 into the tip and pipetting to waste three times. Pipette tips should always be disposed of after pipetting sample or standards.

14.3 Preparing samples

To make 2% HNO_3 add 57 μl 16 N QD HNO_3 to 1943 μl MQ water.

Pick up sample

1. In clean lab take vial of 2% HNO_3 and clean pipette tip.
2. Add 500 μl 2% HNO_3 to each sample vial and leave for 24 hr.
3. Pour samples from vials into cleaned and labelled microcentrifuge tubes.

Transfer samples to Nu lab

1. Place samples in microcentrifuge tube holder inside a clean sample bag.
2. Carry samples directly to the clean cabinet in Nu lab.

14.4 Concentration run

Samples are diluted 100 $\times$ for running to determine concentrations.

Dilute samples

1. Arrange microcentrifuge tubes in order in their stand, with a corresponding row of sample tubes.
2. Number the sample tubes 1-n and record their relation to the microcentrifuge tubes in a lab book.
3. Transfer the microcentrifuge tubes six at a time to the small centrifuge and centrifuge for at least five minutes. This step ensures any resin that has fallen through the frit does not clog the nebulizer.
4. After six samples have been centrifuged, very carefully swap them for any remaining samples and carry them back to the clean cabinet.
5. Take 2 – 20 μl pipette and pipette 5 μl of sample from the microcentrifuge tubes into the corresponding sample tubes - pipette from the top of the sample so as not to disturb any precipitate. Try and place the bead of sample onto an inside edge of the sample tube towards the bottom.

6. Re-cap the microcentrifuge tube, dispose of the pipette tip and repeat for all samples.
7. Once all sample tubes have had sample added, take the 1000 μ l pipette and set it to 495 μ l.
8. Now pipette **495 μ l 2% HNO₃** into each sample tube, ensuring that the beads of HNO₃ entrain the blob of sample stuck to the inside edge of the sample tube.

Prepare NBS 981 Pb standard at 50 ppb

Pb standards are made from a mix of pure Pb standard NBS 891 and a Tl standard. They are mixed such that the beam size for ²⁰⁸Pb is similar to that of the ²⁰⁵Tl beam - because Pb's three isotopes to Tl's two and the relative abundance of each of their isotopes, the beam size is made (roughly) similar by mixing in a ratio 2:1 Pb_{standard}:Tl_{standard}.

1. Take 1000 μ l pipette and set to 1000 μ l.
2. Pipette **2 ml** Pb standard into sample tube and dispose of pipette tip.
3. Take new pipette tip and pipette 1000 μ l 2% HNO₃ to waste.
4. Pipette **1 ml** Tl standard into sample tube and dispose of pipette tip.

Run on Nu

14.5 Diluting samples for run proper

It is best to run samples and standards with the same concentrations of Pb and Tl. The concentrations should be such that a reasonably strong beam is produced, around 7–8 V, which is typically what the 981 standard will give if diluted to 66ppb.

Symbol	Definition
R_{Pb-Tl}	Concentration ratio of Pb to Tl used in the standard and samples (always 2)
D_{cr}	Dilution factor of sample in concentration run
$^{Pb}V_{std}$	Standard's sum Pb beam voltage
$^{Pb}V_{smp}$	Sample's sum Pb beam voltage
$^{20x}V_{std}$	Standard's 20x beam voltage
$^{20x}V_{smp}$	Sample's 20x beam voltage
ν_t	Total volume of solution to be run
ν_{T-smp}^{cr}	Volume of 2% HNO ₃ sample was picked up in for concentration run
ν_t^{cr}	Volume of solution run in the concentration run
ν_{Tl}	Volume of Tl spike to be run
ν_{smp}	Volume of sample to be run
ν_{HNO_3}	Volume of 2% HNO ₃ to be run
$[Pb]_{std}^0$	Concentration of Pb in the stock standard solution (100 ppb)
$[Pb]_{smp}^{cr}$	Concentration of Pb in the sample during concentration run
$[^{20x}Pb]_{std}^{cr}$	Concentration of ^{20x} Pb in standard during concentration run
	= $[Pb]_{std}^{cr} \cdot f_{20x}$, where f_{20x} is the fractional proportion of ^{20x} Pb in the standard
$[^{20x}Pb]_{smp}^0$	Concentration of ^{20x} Pb in sample before dilution
$[Tl]^0$	Concentration of Tl in the stock spike (100 ppb)

Scenario 1. Samples' Pb present at higher concentration than in standard

If the undiluted sample concentration is greater than the standard ²⁰⁸Pb concentration then the following set of equations can be used to calculate dilutions.

To calculate the concentration of ^{20x}Pb in the samples use,

$$[^{20x}\text{Pb}]_{\text{smp}} = \frac{[^{20x}\text{Pb}]_{\text{std}}}{20xV_{\text{std}}} 20xV_{\text{smp}} D_{\text{cr}}.$$

The volume of sample to use in the dilution is calculated by,

$$\nu_{\text{smp}} = \nu_{\text{t}} \frac{\text{Pb}V_{\text{std}}}{\text{Pb}V_{\text{smp}} D_{\text{cr}}}.$$

Note if $\text{Pb}V_{\text{std}}/(\text{Pb}V_{\text{smp}}D) > 1$ then the amount of Pb in the undiluted sample is less than the amount of Pb in the standard. This means the standard will have to be diluted so that Pb is present at a similar concentration to the sample.

Volume of Tl spike is given by,

$$\nu_{\text{Tl}} = \nu_{\text{t}} \frac{[\text{Pb}]_{\text{std}}^{\text{run}}}{R_{\text{Pb-Tl}}[\text{Tl}]^0}.$$

The Volume of HNO_3 to add is then just that required to bring the volume of the three liquids to that of the volume of the solution,

$$\nu_{\text{HNO}_3} = \nu_{\text{t}} - \nu_{\text{std}} - \nu_{\text{smp}}.$$

Scenario 2. Samples' Pb present at lower concentration than in standard

However, if there is more Pb in the 66pb standards than in the samples, it is preferable to run and at as high a concentration as possible. This will mean using all the sample and running just enough to meet the volume requirements of one analysis. Equally, a range of standards will need to be run to in order to match the Pb voltages from each standard.

In order to run the whole sample the uptake rate needs to be known, which will depend upon the particular focusing conditions used on the day.

Determining uptake rate

1. Pipette **1000 μl 2% HNO_3** into a sample tube.
2. Set the Nu to a single run consisting of the number of blocks and ratios which the rest of the samples will be run with.
3. Run the acid under these conditions for one complete analysis.
4. After the analysis is complete, take the 1000 μl pipette and use it to measure out the volume of acid remaining in the sample tube.
5. Uptake volume per analysis, $\nu_{\text{uptake}} = 1000 \mu\text{l} - \nu_{\text{remaining}}$.

With uptake rate known it is possible to calculate the volume of acid to pick the sample up in, given the need for it to be mixed with the Tl spike in a ratio R, to give the volume of fluid drawn in a single run, ν_{uptake} .

The equations to solve are:

$$\nu_{\text{uptake}} = \nu_{\text{Tl}} + \nu_{\text{smp}} \tag{3}$$

$$R_{\text{Pb-Tl}} = \frac{[\text{Pb}]^{\text{cr}}(\nu_{\text{TsmP}}^{\text{cr}} - \nu_{\text{smP}}^{\text{cr}})}{[\text{Tl}]_0 \nu_{\text{Tl}}} \quad (4)$$

where $[Pb]^{\text{cr}} =$

$$\frac{(\sum m_{\text{Pb}}^{208} m_{\text{pb}}^{V_{\text{smP}}}) \cdot D \cdot [\text{Pb}]_{\text{std}}^{\text{cr}}}{\sum m_{\text{Pb}}^{208} V_{\text{std}}} \quad (5)$$

and therefore

$$\nu_{\text{Tl}} = \frac{[\text{Pb}]^{\text{cr}}(\nu_i - \nu_{\text{smP}}^{\text{cr}})}{[\text{Tl}]_0 R_{\text{Pb-Tl}}}. \quad (6)$$

The volume of HNO_3 to pick the sample up in is then just calculated from (3), which also ensures that the total run volume is equal to the uptake rate.

14.6 Post processing of data/offline corrections

14.7 Errors during operation

14.7.1 Unexpected voltage drop

This most frequently occurs when the nebulizer become clogged.

- Put the nebulizer into wash 2.
- Wearing gloves, remove the nebulizer column from its housing in the top of the nebulizer casing.
- Point the column towards your glove, if nitric sprays onto your glove then there may not be a problem with the nebulizer.
- If no nitric is spraying out then the supply tube is clogged. To De-clog the tube force the end of the nebulizer column against your glove, this back flushes the tubes.

14.7.2 00400000: HV3 error

- Go to Monitor:Supplies_monitor, check that there is a voltage on the plate.
- If there is no voltage, try Digital_Control:Power and turning HT off and then on again.
- If turning HT on and off fails, it is necessary to diagnose whether the cable connecting the high voltage transformer is at fault or the transformer itself. To do this swap the connection around between HV3 and HV2, so that the HV3 transformer cable is now supplying the voltage to HV2 and vice versa. If the fault transfers to HV2 then merely the cable is at fault. If the fault remains with HV3 then it is a problem with the transformer itself.

15 Running Samples on the TIMS

15.1 Loading samples

Samples need to be loaded from the beakers they were dried down in, onto tantalum filaments for running under vacuum in the TIMS. Filaments can be prepared six at a time in the loading block.

1. Select six filaments and place them in the testing block.
 - Choose those filaments which have the straightest tantalum wire.
 - If the rods supporting the filament don't allow it to fit inside the hole in the loading block, then gently squeeze the rods together or apart until it fits.
2. Use the voltmeter set to Ω , to test that the filament is an open circuit between filament rods and base.
 - Touch one of the prongs of the multimeter to the base of the filament and the other to the first bar.
 - The multimeter should read 0.L which indicates the circuit is open.
 - If any other reading is displayed replace the filament with another.
 - Repeat this test for the second bar.
3. Test that each filament will take a current across it.
 - Switch the filament dial to "1" on the power pack, and then increase current to **0.8 A**.
 - If the current increases steadily then the filament is cleanly completing the circuit.
 - Turn the current back to 0, switch the filament dial to "2" and repeat. Note that the filament dial records the number of filaments across which there is a voltage, counting from 1. So, "3" means that there is a voltage across the first three filaments.
4. Take the 10 μl pipette and set the dial to 0.7 μl . Clean the pipette tip twice in the vial of MQ water, then pipette to waste **1 μl 1 M H_3PO_4** (phosphoric acid).
5. Pipette **1 μl 1 M H_3PO_4** onto the centre of the tantalum filament.
6. Increase the current to **0.8 A** across all filaments.
7. Take a clean pipette tip (set at 2 μl) and rinse in MQ water twice followed by two rinses in 1 N HCl.
8. Use this pipette to take the sample up in **2 μl 1 N HCl**.
 - Pipette the acid onto the sample and rub the pipette tip around the bottom of the vial to get all the sample into solution.
 - Squirt the sample in and out of the pipette tip a few times to mobilise all the sample. Be careful to avoid generating bubbles.
9. Load **1 μl** of sample onto the filament.
 - Draw **1 μl** of sample into the pipette tip and check that no bubbles have been drawn up.
 - Pipette the drop onto the tantalum filament on the central patch where the phosphoric acid was placed.
 - Pipette any sample remaining stuck to the end of the pipette tip back into the sample beaker and dispose of pipette tip.
 - Close the lid on the sample beaker and write "(1/2)" on its label to indicate that half the sample remains.

10. Dry down the filaments by incrementally increasing the current across all filaments: 1.0 A, 1.3 A, 1.5 A and finally 1.8 A, over 5–10 minutes.
11. Glow the individual filaments.
 - Turn the lights in the cabinet off.
 - Turn the filament dial on the power pack to “1”.
 - Slowly increase the current to **1.8 A**.
 - It might be possible to see some fumes given off, and the residue should turn a dark grey colour.
 - If the filament is not glowing slowly increase the current up to **2.2 A** – when the filament begins to glow, immediately turn the current back down to 0.
 - Repeat for the other filaments, moving each in turn to position 1.
12. Place each filament into a block, screw into place and check that the filament is visible between the slit.
13. Use the metal block to check that the filament rods are spaced correctly, if it does not slide over the rods they will need adjustment.
14. Place the filaments and blocks onto a tray in run order, and place in clean dessicator cabinet.
15. Make a note in the lab book of the sample names and run order.

Part II

Trace element analysis by ICP-MS

Notes

An important point in performing analyses for elemental concentrations is to not lose any sample once the analyte has been weighed out into the teflon vial. This means being careful during the weighing procedure, but also at every step thereafter, such that the sample remains at the bottom of the vial and isn't allowed to get stuck onto the vial lid, or leak out onto the threads.

16 Clean Teflon vials

1. Wipe down the outside of the vials with a kimwipe dampened with MQ, in particular making sure that the threads are clean.
2. Rinse the outside and inside of the vial 3 times with MQ water.
3. Place the vials and lids inside a glass beaker and then pour over **reagent grade HNO_3** and **MQ water** in a 1:1 ratio.
4. Place on a hotplate for at least **1 hr** at **100°C** , so that the acid is boiling.
5. After at least **1 hr**, remove the beaker from the hotplate and allow to cool.
6. Working in the fume cupboard, pour away the HNO_3 and rinse the vials 3 times with **MQ water**, flicking dry afterwards.
7. Half fill the vials with **1% QD HNO_3** and place in the hotblock at **120°C** overnight (or for at least 4 h).
8. After at least 4 h, remove the vials from the hotplate, allow to cool for a few minutes, then pour the **1% QD HNO_3** to waste.
9. Swill the vials once with MQ water, flick dry and then seal.

17 Dry and weigh samples

Aim

Transfer $\sim 1\text{ g}$ of powdered sample to glass jars for weighing and drying, prior to transferring sample to Teflon vials for dissolution.

Notes:

- International rock standards should be prepared with every batch of samples, BCR2 for LREE enriched material, BIR1 for depleted.
- Prepare at least one blank vial (total procedural blank) for every 12 samples.
- Clean the lab surfaces with DI water and Kimwipes before opening any samples. This should include the inside of the fume hood, and the area around the balance.
- Only have one sample open at a time, and clean hands between samples.

17.1 Weigh

1. Place clean Kimwipe down on bench work area.
2. Clean metal scoop/spatula with Kimwipe and DI water and place on Kimwipe.
3. Take clean glass vial and cap, and label each with sample ID - the vial can have a sticky label stuck on it, but the lid needs to be directly written on.
4. Record the mass of the empty vial.
5. Carefully transfer ~ 1 g of powdered sample into the glass vial. Use the cleaned metal spatula, it should take 2 – 3 heaped scoops. Work over the clean Kimwipe on the bench.
6. Re-cap vial and record the vial+sample mass.
7. Clean spatula and work surface, replacing the Kimwipe on the bench with a clean one. Close and store sample vial.

17.2 Dry

1. Turn the oven on to **100°C**.
2. Take the 1l glass beaker and lid, and clean with DI water to remove dust.
3. Lay a Kimwipe on a clean bench surface.
4. Carefully uncap the sample vials, and place the vial into the glass beaker, placing the cap underside down on the Kimwipe.
5. Once the glass beaker contains all the sample, blank and standard vials, cover it with the glass lid and place on the top shelf of the oven with the lip facing towards the door. Leave for ~ 4 hr.
6. Cover the lids with a second Kimwipe to keep dust settling on them.
7. After ~ 4 hr, turn the oven off, open the door and leave the vials to cool (15–20 minutes). Keep as short as possible to avoid the samples re-hydrating.
8. Once cool, re-cap the vials with their appropriate lid, and record their new dried mass.
9. Transfer the vials to a desiccator for storage.

17.3 Weigh sub-sample for dissolution

1. Clean the inside of the scales, remove the balance plate and wipe it down with MQ water. Clean a small metal spatula with Kimwipe and MQ water.
2. Take a clean teflon vial with lid, and place it on the scales zeroing the scales to its mass.
3. Remove the lid, place it beside the vial on the scales and carefully add as close as possible to **0.1 g** of sample using a small metal spatula. Record the added mass.
4. Once the sample has been added, seal the vial and check that no sample powder has spilt on the insides of the balance.

18 Sample dissolution

Aim

Achieve complete sample dissolution in a mixture of HF and HNO₃, followed by gradual evaporation of the HF and replacement by QD HNO₃.

Notes

- Refer to the earlier section for HF safety. For all steps where HF is still present in the sample, follow the HF safety precautions.
- Be careful not to tilt the evaporation elbows too much, else sample could be lost to the collection chamber.

18.1 Procedure

Initial dissolution: addition of HNO_3 and HF

1. Wipe down the inside and outer shelf of the fume cupboard with MQ water.
2. Move the Evapoclean hotblock to the fume cupboard, wipe clean with MQ, and preheat it to **120°C**.
3. Arrange the vials on a Kimwipe inside the fume cupboard, and wipe down their outsides with a Kimwipe dampened with MQ.
4. Opening vials one at a time, pipette **1 ml 16 N QD HNO_3** into to each vial. Swirl gently to ensure an even distribution of the sample in acid.
5. After each sample, check that static hasn't caused any sample to transfer to the pipette tip, your gloves, or the outside of the sample vial; if it has, clean/dispose of the contaminated surface. Replace the Kimwipe if it had any nitric spilt on it.
6. Using a clean pipette tip, pre-washed with HF, add **4 ml 40% HF** to each sample.
7. Place vials in the Evapoclean hotblock at **120°C** for **24 hr** to digest.

Evaporation: Stage 1

1. After 24 hr, remove the samples from the Evapoclean hotblock and allow to cool for 10 minutes.
2. Reduce the temperature of the Evapoclean hotblock to **100°C**.
3. Take the necessary number of evaporating elbows, check they are all clean, and line them up inside the fume cupboard on a Kimwipe.
4. Remove the vial lid and place on clean Kimwipe in the fume cupboard; screw the vial into an elbow and place the elbow (sample vial first) into the side compartments of the Evapoclean hotblock.
5. Leave for **2–4 hr**, so that the HF evaporates into the collection vial, the sample should be left as a large drop at the bottom of the vial. Do not allow all the acid to evaporate.

Evaporation: Stage 2

1. After **2–4 hr** remove the vials to the elbow stand and leave to cool for 10 minutes.
2. Once cool, unscrew each of the collection vials and pour the evaporated HF and HNO_3 to waste, reattaching the collection vials straight after.
3. Next, unscrew the sample vials and add **1 ml 16 N QD HNO_3** to each, re-screwing the vial into the elbow after each acid addition, and placing back into the Evapoclean hotblock.
4. Leave for **1–2 hr**, until the sample has dried to a large drop. Do not allow all the acid to evaporate.

Evaporation: Stage 3

1. After **1–2 hr** remove the vials to the elbow stand and leave to cool for 10 minutes.
2. Once cool, unscrew each of the collection vials and pour the evaporated HF and HNO₃ to waste, reattaching the collection vials straight after.
3. Next, unscrew the sample vials and add **1 ml 16 N QD HNO₃** to each, re-screwing the vial into the elbow after each acid addition, and placing back into the Evapoclean hotblock.
4. Leave for **1–2 hr**, until the sample has dried to a large drop. Do not allow all the acid to evaporate.

Pick-up

1. After the samples have dried to a large drop, remove them from the hotblock and allow to cool.
2. Once cool, add **2.5 ml 16 N QD HNO₃** to each vial using a clean pipette, followed by a squirt of MQ water to bring the level in the vial up to half way. Tightly cap the vials with their original lids.
3. Replace the vials on the hotblock at **100°** for **~ 3 hr**.
4. After **~ 3 hr**, check that no white fluoride precipitates remain in the vials. If there are still precipitates, add **5–10 ml MQ water** and heat until the solutions clear.

19 Dilution and transfer to LDPE bottle

Aim

Once the sample is fully dissolved, it needs to be transferred to a larger LDPE bottle for further dilution ready for analysis.

19.1 Procedure

1. Take a pre-cleaned **60 ml** LDPE bottle, remove its lid and place the lid on a kimwipe on the bench. (To clean an uncleaned LPDE bottle, rinse first with MQ water, followed by a 2% HNO₃ rinse.)
2. Uncap the beaker, and place it on the analytical balance and zero.
3. Remove the beaker from the balance and carefully pour in the sample.
4. Rinse the sample vial 3 times with **MQ water**, after each rinse pour the MQ water into the LDPE bottle. With the MQ washes, swill the water around the inside of the vial, picking up any remaining sample on the inside of the lid and vial walls.
5. Return the beaker to the balance and wait for it to settle.
6. Using the squeezezy bottle dispenser **slowly** add **MQ water** to bring the mass as close as possible to **50.0000 g**. Record the final mass of the solution in you notebook. The sample has now been diluted to **~ 3.5% HNO₃** in **~ 50 ml**.

Part III

Major and trace element analysis by XRF - performed in Edinburgh

Notes

Two disks are made for analysis, a glass disk for analysis of the major elements and a pressed powder pellet for analysis of the trace elements. There is a grain size effect in the fluorescence of x-rays from the source material, which diminishes with decreased grain size. In the limit the sample material can be fused into a glass to reduce this effect as much as is possible, this is done for the material analysed for major elements.

The Rh anode in the Edinburgh XRF makes it particularly precise for Rb, Sr, Y, Zr, Nb and Mo as the Rh K lines are able to excite emission from these elements.

La_2O_3 is added to the flux ($\text{Li}_2\text{B}_4\text{O}_7$ and Li_2O , which is added to the sample in a fixed ratio) in order to reduce the effect of absorption and tertiary x-ray emission during major element analysis. The addition of a heavy absorber essentially reduces the proportional matrix difference between samples owing to varying amounts of Fe, Ca etc. The addition of a heavy absorber reduces x-ray intensities and is thus inappropriate for trace element analysis. Mathematical correction for absorption in the major elements is still applied however.

For a more thorough description of XRF principles and applications see Fitton (1997).

20 Cleaning of lab materials

Pt crucibles

Cleaned overnight in hot HCl, and rinsed before use in DI water.

Spatulas and other apparatus

Wiped down with damp tissues, tap water is fine, air dry if possible.

21 Glass disk preparation for major element analysis

Aim

To produce a homogeneous glassy sample disk of known mass for analysis.

notes

Prepare samples in batches of **8**, this is the number of platinum crucibles that can fit into the furnace tray. An example of how the weights should be recorded is given in table 6 below.

At all stages avoid the Pt crucibles coming into contact with the iron tongs, and the reducing part of the Merkel burner flame.

Glass disks have a finite lifespan as they slowly de-vitrify.

21.1 Procedure

Table 6: Example of how data should be recorded when manufacturing the major element glass disks. UNIG stands for Un-ignited, IG for ignited, LOI for loss on ignition.

Sample No.	BOL-09-1	...
Crucible No.	1	...
Crucible (C), g	17.8981	...
Crucible + Sample (UNIG), g	18.8386	...
Crucible + Sample (IG), g	18.8435	...
Sample (S = UNIG – C), g	0.9405	...
Flux (F = S * 5), g	4.7025	...
Total (T = UNIG + F), g	23.5411	...
LOI(%) = 100 * (UNIG – IG)/S	-0.52	...

1. Transfer **2 ± 0.1 g** of sample powder into a labelled glass vial using a clean metal spatula.
2. Dry the samples in an oven set at **110°C** for at least **2 hr**.
3. When dried, move the samples directly from the oven into a desiccating chamber, and move the desiccating chamber over to the precise balance area.
4. Prepare one cleaned Pt crucible for each sample (up to the maximum 8), and order on the granite slate. At this point maintaining a consistent sample order is vital, as the Pt crucibles are only very faintly marked.
5. Zero the scales then record the weight of the first Pt crucible (to four decimal places).
6. Precisely weigh **0.95 ± 0.01 g** of sample into the Pt crucible, being careful to avoid spilling any sample on the balance. Sample is best transferred by pouring directly from the glass vial, tapping it to add small amounts. If too much sample is added, use the narrow spatula to remove sample until the requisite mass is obtained.
7. Record the new **sample + crucible** weight.
8. After all samples have been added to their corresponding Pt crucible and their weight's recorded, transfer the crucibles onto a ceramic tray (being careful to preserve the sample order) and place Pt lids on each crucible. Place the samples into the furnace at **1100°C** for **20 minutes**.
9. Whilst the samples are being fused, calculate the total mass of the crucible after flux has been added, = (un-ignited sample + crucible mass) + flux, where flux = 5 * Sample mass, ready for step 12.
10. After **20 minutes**, remove the samples from the furnace and allow to cool.
11. Once cool, re-weigh the crucible and record the new mass (this information is used to calculate LOI, loss on ignition).
12. Now add Johnson Matthey Spectroflux®, using a 5:1 sample:flux dilution, where sample mass is the un-ignited sample mass. Use the narrow spatula to add the flux, be precise to **±0.0001 g**.
13. Once the flux is added, using a metal spatula carefully prise the fused sample off the bottom of the crucible and shift it into the middle of the flux. This ensures that the flux is surrounding the sample and that it melts fully.
14. After adding flux to all the samples, place them back in the furnace with lids on at **1100°C** for **20 minutes**.
15. **20 minutes** later, remove the crucibles and allow to cool.

16. Re-weigh the crucibles, and accurately (to within 0.0001 ± 0.1 g) add flux to bring the total mass up to the calculated total mass (there will have been a mass loss on fusion due to the loss of adsorbed water from the flux, which needs to be compensated for).
17. Ignite the two Meker burners and turn on the hotplate to **220°C**.
18. Take two samples with lids on over to the Meker burners and place them over the flame, suspended by the ceramic supports. There are Pt tipped tongs for transferring the crucibles to and from the flames. Make sure that after transferring onto the burners that the lids are placed back over the crucibles as soon as possible to avoid the sample popping out in response to the heat shock.
19. After a minute, take off the lid and swirl each sample for ~ 30 s to ensure homogeneity. **Perform this step twice.**
20. Prepare a graphite plate with surrounding steel ring on the hotplate, and move it close to the Meker burner.
21. When ready, swirl the sample above the flame a final time before quickly pouring it into the centre of the graphite plate ensuring as much sample as possible is transferred (a bead will always be left), then as soon as possible lower the aluminium plunger onto the globule of molten sample to flatten it into a disk. Leave the plunger on the disk for at least **30 s**.
22. Replace the crucible with remaining sample onto the burner to re-melt it. Have a litre beaker of tap water ready, then once the sample bead is molten use the tongs to tip the remaining sample into the water (tapping against the edge of the beaker to dislodge it) then drop the crucible in.
23. Return to the pressed sample disk and remove the aluminium plunger and steel ring, quickly covering the sample with an upturned petri-dish (this ensures the rate of cooling isn't so high that it cracks the disk).
24. Repeat the above steps for the remaining samples, transferring them across to the Meker burners in pairs.
25. The glass disks should be left to anneal on the hotplate at **220°C** for at least **5 minutes**.
26. Once annealed, the glass disks can be upturned out of the graphite plates, excess glass carefully clipped off using a pair of pliers, and a sticker stuck on the non-analysis side (the side that contacted the plunger).

22 Pressed pellet preparation for trace element analysis

Aim

To produce a clean pressed pellet (38 mm disk) of sample for analysis. Mass does not need to be as precisely known for trace elements as the disks are semi-infinite with respect to x-ray penetration.

22.1 Procedure

1. Weigh out **8.0 ± 0.1 g** of rock powder into a clean beaker.
2. Shake the surface of this powder level, and add **8** drops of polyvinyl alcohol (PVA, 2% aqueous solution), which acts as a binding agent. The drops should form separate spots on the sample surface.
3. Shake the powder again to cover the PVA drops and then stir with a glass rod until fully mixed.
4. Construct the steel compression apparatus with one tungsten carbide disk in place and slide down an aluminium capsule on top of it.
5. Carefully scrape and pour as much of the sample as possible into the aluminium capsule using a metal spatula. An inner steel sleeve should be put in place to prevent the sample overspilling the aluminium capsule.
6. Slowly insert the perspex rod into the compression mould, smooth end first, to initially smooth the surface of the powder by gently rotating it, and then push down once to compress the sample powder.
7. Slowly remove the perspex rod and scrape any sample adhered to it back onto the sample disk using a metal spatula.
8. Slowly remove the steel sleeve and scrape any sample adhered to it onto the sample disk.
9. Run a narrow metal spatula around the inner edge of the aluminium capsule, to produce a groove in the sample powder pushing it away from the capsule edge. This ensures that sample doesn't move up the sides of the apparatus during compression.
10. Assemble the remainder of the compression apparatus; dropping the second tungsten carbide disk down onto the sample and placing on top of this the steel compression rod.
11. Place this entire apparatus inside the press and apply **8 tons** over **2 minutes**.
12. Afterwards, invert compression mould and remove the steel base and tungsten carbide disk - label the back of the aluminium sample casing.
13. Clean and dry all sample compression apparatus with warm water. Acetone can be used to clean the tungsten carbide disks.

Part IV

Mounting crystals and glasses

23 Mounting sample material

Aim

Isolating preferred material and mounting it in resin, polishing to finish as a function of analysis routine (ion probe requires a better polish than EPMA, which requires a better polish than the laser, which is tolerant of pretty uneven surfaces).

23.1 Picking

1. Sieve material into specific size fractions before picking. Very fine material ($< 200\mu\text{m}$) is hard to pick from and obscures larger crystals.
2. Pick using a binocular microscope with sample material of a particular size fraction poured into a clean petri dish, and using a fine pair of tweezers.
3. Clean the area around the microscope and place down clean white paper, this way any crystals bouncing out of the dish can be easily spotted, identified as being from the sample, and put back in.
4. Pick in two stages: first into a separate container for the particular crystal type, then re-pick that picked fraction for specific requirements (size, presence of melt inclusions etc.).
5. Olivines will look light yellow/green, sometimes more brown if they have a glassy coating or are very fayalitic. Clinopyroxene will have a strong green colour if it has reasonably high chrome content, otherwise is black, and will fracture along cleavage. Very thin fragments of crystal can be hard to distinguish from each other and glass. Glass will in general be more transparent than clinopyroxene and browner, with conchoidal fractures.

23.2 Mounting

1. Prepare a perspex base, ~ 5 cm square. Edges will need cleaning off with a knife and the surface should be wiped down so it is smooth and clean.
2. Draw a circle the diameter of the mounting cylinders onto the clear side of the perspex base using a permanent marker. For trace element or EPMA analysis this circle will be the outline into which crystals will be placed. For isotope work draw a second circle centred within the large circle of ~ 1 cm diameter. There are edge effects associated with analysing near the perimeter of the stub which can manifest when making very sensitive measurements.
3. Place double sided sticky tape onto the clear side of the perspex base, over the circle. Two strips will be needed, make sure they touch (but don't overlap) so that no resin will leak onto the perspex.
4. Pick crystals onto the double sided sticky tape.
 - Make sure to orientate crystals for optimal exposure of the relevant features.
 - Crystals can be close together, but avoid the final couple of millimetres before the disk's edge. For ion probe work, especially if oxygen isotopes are going to be measured, only place crystals in the very centre of the disk.

23.3 Adding resin

Use EpoThin[®] resin as it has a low viscosity, and is appropriate for use in the ion probe.

1. Clean the inside of the resin mould and outer flange of any previous resin or dirt, cleaning the latter will ensure the seal with the base will be tight.
2. Coat the inside edge of the resin mould (plastic cylinder) with the release agent and allow to dry.
3. Once the release agent has dried, firmly press the plastic mould onto the double sided sticky tape over the marked circle flanged side down.
4. Seal the rim of the mould onto the perspex base by placing blue-tack all around the mould's perimeter.
5. Mix the resin with hardener in the mass ratio of **3 : 1.17** (4.17 g of mixed resin makes 1 stub).
6. Stir until all streakiness disappears and the resin is homogeneous, avoid introducing air bubbles by stirring slowly. If there any air bubbles try and remove them with the stirring rod.
7. Slowly pour the mixed resin into the mould
 - Fill from an edge to avoid trapping bubbles on the crystals.
 - Pour very slowly, use a thin glass rod to shear the resin as your pour it to remove bubbles.
 - Fill up to a maximum height of ~ 5 ml unless the sample is particularly large - more resin means more degassing and a worse vacuum in the probe.
8. Cover the top of the mould and leave the resin to set for at least **3 days**.

23.4 Polishing

The stub will take on a better polish if it has been left to fully harden. The most important thing at this stage is not to cross contaminate polishing grades, so work as cleanly as possible.

1. Begin polishing using emery paper, start at 400, then move onto 800, 1200, and finally 2500.
2. At this stage, the engraving pen can be used to mark the sample name on the edge of the disk.
 - Wash the emery paper under a tap before use to remove any coarser material.
 - Place the paper on a flat surface, special thickened square of glass are good.
 - Wet the paper and polish down the sample, it will probably only need half a minute to a couple of minutes at this stage. Wet paper will take more off than dry emery paper.
 - Wash sample, emery paper and glass plate in-between each polishing grade to avoid cross contamination.
3. After 2500 emery paper move onto the diamond polishing paste. Start at $9\mu\text{m}$ (red) and then $6\mu\text{m}$ (yellow), $3\mu\text{m}$ (green) and $1\mu\text{m}$ (white) if necessary (e.g. ion probe work).
 - Avoidance of cross-contamination at this stage is vital. Ultrasonicate the stub in clean water for at least 20 minutes before moving to this stage from emery paper, and repeat between each step down in diamond size.
 - Check under a binocular microscope that all holes in the stub are clean of carbide before moving to the diamond pastes. If they are not, clean them out with tweezers or a brush and re-ultrasonicate.
 - Find the correct soft mat polisher and make sure it is the right size for your polishing (use colour of disk to determine if not labelled).

- Lightly wet the disk with DI water and add a few drops of diamond paste.
 - Begin by polishing the reverse of the stub, this way if the pad is contaminated you can tell without damaging the sample.
 - Use a reflected light microscope to judge degree of polish, when all the scratches are continuous and of the same width then you have probably polished to the optimum with that particular paste.
 - Ultrasonicate for 10 minutes and move onto the next grade down.
4. Once polished to the desire level, ultrasonicate a final time to remove the paste and store in a clean environment.

Part V

Data and reference material

24 Processes within the mass spectrometer

To understand the limitations and uncertainties in data obtained from using the Nu, one should know how and why the voltages of beams reported by the detectors may deviate from the true isotopic abundances in the sample. This requires an appreciation of the processes that take a dissolved sample from the beaker and result in a series of voltages measured in the collectors. These processes are discussed briefly in this section, the final conversion of those voltages to a series of ratios is dealt with in the subsequent section. A slightly more detailed introduction is contained in the Nu user's manual and Belshaw et al. (1998).

A cartoon of the Nu's setup is provided in Fig. 1. Sample introduction, ionisation and analysis proceeds as follows,

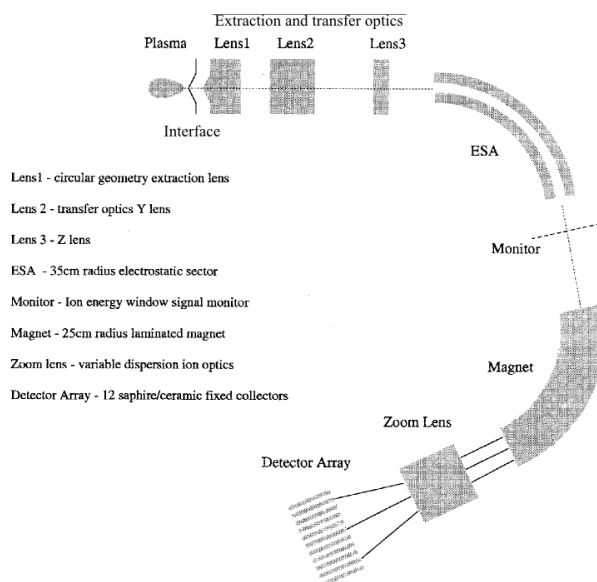


Figure 1: Schematic of Nu plasma, modified from Belshaw et al. (1998). ESA=Electrostatic Analyser.

1. **Sample introduction:** This is carried out by the desolvating nebulizer. It uptakes sample from its sample vial and removes the solvent (desolves) from the solution, such that only the analyte elements remain. Desolvation is achieved by heating the aerosol in argon to evaporate the solvent. The dry sample aerosol is then swept into the plasma and ionised. Matrix effects can influence the processes occurring at this stage, as sample composition will govern how the analyte elements complex.
2. **Sample ionisation:** Following solvent removal the sample is introduced to the plasma with the carrier argon gas. The plasma is kept at above $5000^{\text{circ}}\text{C}$, sufficient to cause most of the sample to first atomize and then ionize. Efficiency approaches 100% (although in detail is a function of the ionization potential of an element), so that little fractionation between isotopes is envisaged to occur at this stage. Ionization occurs at atmospheric pressure, and from this point the vacuum systematically improves along the flight path.
3. **Interface region:** This section consists of a Ni sampler cone, located next to the plasma, and behind this a Ni skimmer cone at 4 kV. Each cone has a ~ 1 mm hole through which some of the

ions pass. At this stage mass fractionation can occur from space charge effects, as lower mass ions will have been deflected to the edge of the beam, which is the portion preferentially skimmed off by the two cones. Consequently the more of a beam that is lost from skimming both on these and subsequent lenses, the greater the bias towards the heavy isotope.

4. **Extraction and transfer optics:** The plasma is then passed through a series of lenses forming the extraction optics, which allow the passage of a circular cross section of the beam to pass onto the transfer assembly. In the transfer optics the beam is converted from a circular to slit cross section, the geometry of beam required to enter the mass analyser.
5. **The Electrostatic analyser:** Ions entering the quadrupole will travel along trajectories that are a function of mass and energy, this means that ions of the same mass will not be focused to the same point if they have different energies, blurring the resolution of the mass spectrometer. To counter this the electrostatic analyser (ESA) is introduced along the ion path before they arrive at the magnet. The ESA consists of two plates held at a voltage, generating an electric field in the space in-between them. Ions passing into this region are deflected according to their energy, independently of their mass, with high energy ions on the outside and low energy on the inside. Neutrals, or ions with very high or low energies will impact the walls and thus be filtered out of the beam altogether. The remaining energy range of ions results in their being focused to different points, but solely as a function of their energy in contrast to the quadrupole. The positions of the focal points can be thus be tuned to compensate for the smearing of the image in the magnet. A set-up of this kind, with focusing provided both from an ESA and quadrupole is called double focusing.
6. **Quadrupole magnet:** At this stage ions are separated by mass according to their deflection in the magnetic field. Leaving the quadrupole, the different masses of ions are focused into discrete beams.
7. **Zoom lens:** The zoom lens consists of a pair of quadrupole lenses which act to control the magnification of the image. This step is necessary to have the beams incident on the centre of the Faraday collectors, as the collectors are static the beams themselves have to be adjusted. The problem arises masses will have been separated by different amounts on leaving the quadrupole. The separation achieved between ^{204}Pb and ^{208}Pb for example, is much smaller than between lower mass isotopes.
8. **Faraday cup collector array:** When the positively charged ions impact the Faraday collector electrons flow to neutralise the charge imbalance. This flow of electrons generates a measurable current (if enough ions are impacting the collector) and it is the relative strength of this signal between cups which ends up giving an isotopic ratio of the sample.

25 Processing of data: online and offline corrections

The Nu outputs a file with one row of numbers for each sample analysed. These numbers, which consist of average corrected isotopic ratios, averaged internal errors and some averaged almost-raw beam intensities, are derived from the raw beam voltages through the application of a number of corrections. The series of events through which the raw beam voltages are converted into single corrected ratios is as follows,

1. **Perform baseline subtraction:** At the beginning of each block the Nu measures the offset of the Faraday cups' voltage from zero. These offsets are subtracted from each subsequent voltage measured in the block. At the end of the block the Nu re-measures the baseline.
2. **Correct for ^{204}Hg interference (Pb only):** ^{204}Hg interferes with measurement of ^{204}Pb , a generally small effect, but pronounced if the samples being run contain very small quantities of Pb. Measured ^{202}Hg is corrected for mass dependent fractionation (from Tl fractionation), so that the

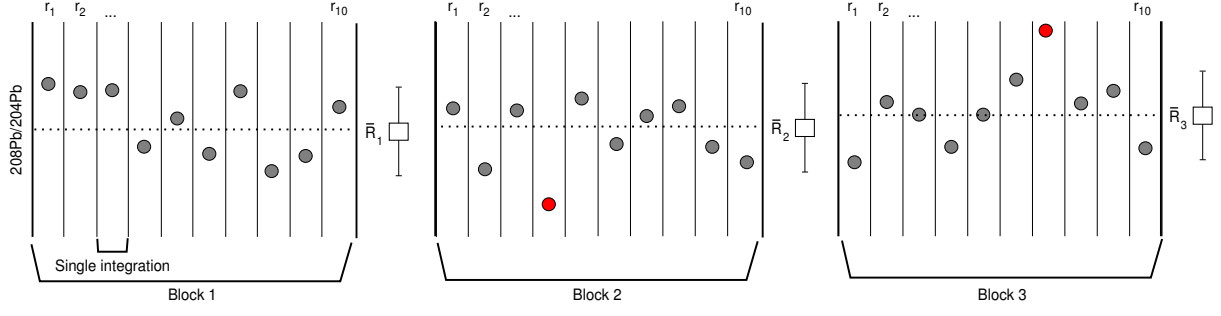


Figure 2: Schematic of the measurements made by the Nu in a single sample run. Depicted is the process whereby initial isotopic ratios (themselves the product of integrating beam intensities over a few seconds) are combined over several integrations into a block of measurements, and several blocks are averaged to produce a single ratio. At the end of each block, an average and standard deviation is calculated.

known natural ratio of $^{204}\text{Hg}/^{202}\text{Hg}$ can be used to calculate the voltage from ^{204}Hg isobarically interfering with measurement of ^{204}Pb .

3. **Correct for ^{204}Hg interference (Nd only):**

4. **Correct for mass dependent fractionation (Pb only):** Now each individual integration can be corrected for mass dependent fractionation using the measured $^{205}\text{Tl}/^{203}\text{Tl}$ voltage ratio at the time that integration was made. The deviation of this ratio from the known value is attributed to mass dependent fractionation and constrains the fractionation factor during that integration. The mass dependent fractionation is then assumed to be the same between Tl and Pb, thus the fractionation factor calculated for Tl is applied to the Pb isotope measurements in order to correct them, using the exponential law.

5. **Correct for mass dependent fractionation (Nd only):**

6. **2 sigma test:** The ratios from all integrations within a block are used to define means and standard deviations. Ratios lying outside two standard deviations are rejected and the remainder included for the average ratio calculations, red points in Figure 2. This is repeated for all blocks in an analysis.

7. **Final ratio:** A final mean isotopic composition from the sample is obtained from an average of the integrations that passed the 2σ test.

The remaining correction to be applied is offline and compensates for the difference between the value the standard ran at and the true composition of the standard. This is done by either sample bracketing or using a run average.

26 Error on results

Calculation of ppm error on ratio R from 2σ external error on R,

$$2\sigma_{\text{ppm}} = \frac{2\sigma_R}{R} \cdot 10^6.$$

27 Standard values

Contained in table 10 are the isotopic compositions assumed, measured, or specifically determined, in various standard solutions as reported in a number of studies.

Table 7: **Standard values, (as) assumed value, (m) measured value, (eq) an equivalent value - having reported relative to another reference value, (det) specific determination of standard composition**

Material	Ratio	Value	Type	Reference
La Jolla	$^{143}\text{Nd}/^{144}\text{Nd}$	0.511835	as	Schilling et al. (1999)
		0.511856	as	Thirlwall et al. (2004), Aldrich mean
		0.511860	as	Abouchami et al. (2005)
		0.511872	as	Cordier et al. (2010) as of Nauret et al. (2006)
		0.511850	as	Ingle et al. (2010)
JNdi-1	$^{143}\text{Nd}/^{144}\text{Nd}$	0.512115	det	Tanaka et al. (2000)
NIST SRM 981	$^{208}\text{Pb}/^{204}\text{Pb}$	36.7213	det	NIST cert. (1973)
		36.7006	det	Todt et al. (1996)
		36.7219	det	Galer and Abouchami (1998)
	$^{207}\text{Pb}/^{204}\text{Pb}$	36.722	eq	Thirlwall et al. (2004)
		15.49135	det	NIST cert. (1973)
		15.4891	det	Todt et al. (1996)
	$^{206}\text{Pb}/^{204}\text{Pb}$	15.4963	det	Galer and Abouchami (1998)
		15.4980	eq	Thirlwall et al. (2004)
		16.937096	det	NIST cert. (1973)
	$^{208}\text{Pb}/^{204}\text{Pb}$	16.9356	det	Todt et al. (1996)
		16.9405	det	Galer and Abouchami (1998)
		16.9408	eq	Thirlwall et al. (2004)
NIST SRM 982	$^{208}\text{Pb}/^{204}\text{Pb}$	36.74492	det	NIST 1968
		36.7555	det	Todt et al. (1996)
	$^{207}\text{Pb}/^{204}\text{Pb}$	17.15970	det	NIST 1968
		17.1621	det	Todt et al. (1996)
	$^{206}\text{Pb}/^{204}\text{Pb}$	36.739043	det	NIST 1968
NIST SRM 983	$^{208}\text{Pb}/^{204}\text{Pb}$	36.7492	det	Todt et al. (1996)
	$^{208}\text{Pb}/^{204}\text{Pb}$	36.708895	det	NIST cert. (1968)
	$^{207}\text{Pb}/^{204}\text{Pb}$	191.716	det	NIST cert. (1968)
Eimer and Amend (E&A) NIST SRM 987	$^{206}\text{Pb}/^{204}\text{Pb}$	2695.41779	det	NIST cert. (1968)
	$^{87}\text{Sr}/^{86}\text{Sr}$	0.708000	as	Schilling et al. (1999)
		0.71034	det	NIST cert. (2007)
		0.710248	as	Thirlwall et al. (2004)
		0.710250	as	Abouchami et al. (2005)
		0.71024	as	Cordier et al. (2010) as of Nauret et al. (2006)
		0.710238	m	Ingle et al. (2010)
		0.71025	as	Peate et al. (2010)

28 Composition of common phases

Table 8: **Common phases, (as) assumed composition, (det) specific determination of composition**

Phase	Ratio	Value	Type	Reference
Broken Hill	$^{208}\text{Pb}/^{204}\text{Pb}$	35.675	as	Doe et al. (1985)
		35.65	as	Rudnick and Goldstein (1990)
	$^{207}\text{Pb}/^{204}\text{Pb}$	15.389	as	Doe et al. (1985)
		15.39	as	Rudnick and Goldstein (1990)
	$^{206}\text{Pb}/^{204}\text{Pb}$	16.003	as	Doe et al. (1985)
		16.00	as	Rudnick and Goldstein (1990)

29 Composition of the solid earth

Table 9: **Isotopic composition of solid earth materials, (as) assumed composition, (det) specific determination of composition**

Element	Ratio	Value	Type	Reference
Chondritic Nd	$^{143}\text{Nd}/^{144}\text{Nd}$	0.512638	det	Jacobsen and Wasserburg (1980)
		0.51264	as	Ingle et al. (2010)
		0.512638	as	Blichert-Toft and Albarède (2009)
Terrestrial Hg	$^{204}\text{Hg}/^{202}\text{Hg}$	0.2299	det	Zadnik et al. (1989)

30 Atomic masses

Table 10: **Atomic masses, as used in mass fractionation corrections by the Nu**

Element	Isotope	Mass	Reference
Pb	204	203.973037	-
	206	205.974455	-
	207	206.975885	-
	208	207.976641	-
Tl	203	202.972336	-
	205	204.97441	-

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